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**Symposium on Environmental Transport and Transformation  
of Pesticides: Joint U.S.-U.S.S.R. Project 02.03-31  
'Forms and Mechanisms by Which Pesticides and  
Chemicals are Transported'**

**Environmental Research Lab., Athens, Ga.**

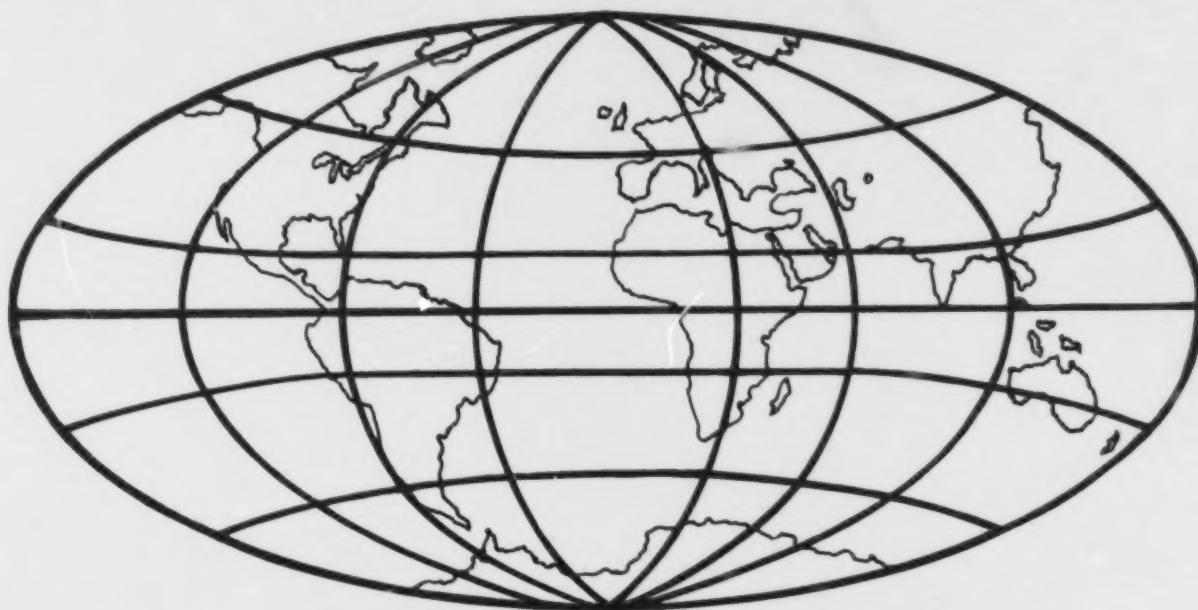
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# SYMPOSIUM ON ENVIRONMENTAL TRANSPORT AND TRANSFORMATION OF PESTICIDES



OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY

Environmental Research Laboratory  
Athens, Georgia 30605

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SYMPOSIUM  
ON

ENVIRONMENTAL TRANSPORT AND TRANSFORMATION OF PESTICIDES

JOINT U.S.-U.S.S.R. PROJECT 02.03-31  
"FORMS AND MECHANISMS BY WHICH PESTICIDES AND CHEMICALS ARE TRANSPORTED"

S. G. Malakhov, Co-Chairman, U.S.S.R. Side  
David W. Duttweiler, Co-Chairman, U.S. Side

ENVIRONMENTAL RESEARCH LABORATORY  
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## FOREWORD

Cooperation and exchange of scientific information under the US-USSR Agreement on Cooperation in the Field of Environmental Protection has helped both countries in their efforts to control environmental pollution. Begun in 1972, the Agreement was extended for a second 5-year period by the Co-Chairmen of the Joint US-USSR Committee--Mr. Douglas M. Costle, Administrator for the U.S. Environmental Protection Agency, and Academician Yuri Z. Izrael, Chief of the Main Administration of the Hydrometeorological Service.

Among several working groups and projects established under this Agreement is Project 02.03-31, "Forms and Mechanisms by Which Pesticides and Chemicals are Transported in Soil, Water, and Biota." The agreed objective of this project is "mutually beneficial cooperation that will aid in the solution of environmental problems associated with the migration of pesticides and chemical substances used in agriculture." Responsibility for US participation in the joint project was assigned to the undersigned in 1974. Members of this project and invited experts from government research organizations, academia, and private industry from the two countries have since exchanged visits on several occasions. This document records the extended abstracts of papers presented at a project symposium, which was held in October 1976 in Tbilisi, USSR, to exchange current scientific information on the environmental movement and transformation of agricultural pesticides.

David W. Duttweiler  
Director  
Environmental Research Laboratory  
Athens, Georgia

# ABSTRACT

Under the USA-USSR Agreement on Cooperation in the Field of Environmental Protection, a joint project committee on environmental transport of agricultural chemicals (pesticides and fertilizers) sponsored a symposium on 20-27 October 1976 in Tbilisi, USSR. Papers were presented by American and Soviet scientists on the movement and transformations of pesticides in the atmosphere, in soils, in water, in plants, and in animals, and on the use of mathematical modeling to describe the transport and transformation of pesticides in the environment. Twenty-six papers encompassed reviews of the state of the art in each country and results of research on particular aspects of the topics.

## CONTENTS

|                                                                 |      |
|-----------------------------------------------------------------|------|
| Foreword . . . . .                                              | iii  |
| Abstract . . . . .                                              | iv   |
| Introduction . . . . .                                          | viii |
| Pesticide Movement and Transformation in the Atmosphere         |      |
| Co-Chairmen: D. G. Crosby (USA) and S. G. Malakhov (USSR)       |      |
| Atmospheric Transport and Transformation of Pesticides. . . . . | 1    |
| D. G. Crosby, University of California                          |      |
| Atmospheric Transport of DDT. . . . .                           | 11   |
| V. A. Borzilov, S. G. Malakhov, and A. I. Osadchii,             |      |
| Institute of Experimental Meteorology; V. M. Koropalov          |      |
| and I. M. Nazarov, Institute of Applied Geophysics              |      |
| Disparlure and Some Juvenile Hormone Analogue Persistence       |      |
| in the Environment . . . . .                                    | 21   |
| F. P. Waintraub, G. F. Vylegzhanina, L. L. Chernichuk,          |      |
| and I. A. Konjukhova, All-Union Institute for                   |      |
| Biological Methods of Plant Protection                          |      |
| Pesticide Transport and Transformation in Soil                  |      |
| Co-Chairmen: D. D. Kaufman (USA) and M. S. Sokolov (USSR)       |      |
| Predicting and Simulating Pesticide Transport from Agricultural |      |
| Land: Mathematical Model Development and Testing. . . . .       | 30   |
| G. W. Bailey and H. P. Nicholson, U. S. Environmental           |      |
| Protection Agency                                               |      |
| General Laws of the Migration of Pesticide Residues in the      |      |
| Delta Landscape under Irrigation . . . . .                      | 38   |
| M. S. Sokolov, Institute of Agrochemistry and Soil              |      |
| Science of the USSR Academy of Sciences                         |      |
| Certain Laws of Organochlorine Pesticide Redistribution         |      |
| in the Soil-Water, Soil-Plant System . . . . .                  | 47   |
| G. G. Zhdamirov, E. E. Popov, and N. F. Lapina,                 |      |
| Institute of Experimental Meteorology                           |      |

# CONTENTS (continued)

|                                                                                                                                                                                 |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Pesticide Transport and Metabolism in Model Systems . . . . .                                                                                                                   | 61  |
| D. D. Kaufman, P. C. Kearney, and R. G. Nash,<br>U. S. Department of Agriculture                                                                                                |     |
| Cometabolism of Foreign Compounds . . . . .                                                                                                                                     | 73  |
| L. A. Golovleva and G. K. Skryabin, Institute<br>of Biochemistry and Physiology of Microorganisms                                                                               |     |
| On the Estimation of the Anthropogenic Pollution Effect<br>on the Functional State of the Soil Microflora . . . . .                                                             | 86  |
| E. I. Gaponyuk and V. A. Kobzev, Institute of<br>Experimental Meteorology                                                                                                       |     |
| Pesticide Transport and Transformation in Water<br>Co-Chairmen: G. L. Baughman (USA) and M. N. Tarasov (USSR)                                                                   |     |
| Transformation and Transport Processes in Aquatic Systems . . . . .                                                                                                             | 98  |
| G. L. Baughman, U. S. Environmental Protection Agency                                                                                                                           |     |
| Estimation of Organochlorine Pesticide Loss in Surface<br>Runoff Waters. . . . .                                                                                                | 103 |
| Ts. I. Bobovnikova, E. P. Virchenko, G. K. Morozova,<br>Z. A. Sinitsyna, and Yu. P. Cherkhanov, Institute of<br>Experimental Meteorology and Institute of Applied<br>Geophysics |     |
| Hexachlorocyclohexane, Metaphos, and Chlorophos Decomposition<br>in Soil and Their Migration with the Waters of Surface<br>Runoff . . . . .                                     | 108 |
| M. N. Tarasov, L. G. Korotova, A. S. Demchenko, and<br>L. V. Brazhnikova, Hydrochemical Institute                                                                               |     |
| Partitioning and Uptake of Pesticides in Biological Systems . . . . .                                                                                                           | 117 |
| E. E. Kenaga, Dow Chemical U.S.A.                                                                                                                                               |     |
| Pesticide Transport and Transformation in Plants<br>Co-Chairmen: J. J. Menn (USA) and F. P. Waintraub (USSR)                                                                    |     |
| Pesticide Transport and Transformation in Plants. . . . .                                                                                                                       | 126 |
| D. S. Frear, U. S. Department of Agriculture,<br>and J. J. Menn, Stauffer Chemical Company                                                                                      |     |
| Pathways of Pesticide Dissipation and Decomposition . . . . .                                                                                                                   | 140 |
| F. P. Waintraub, G. F. Vylegzhanina, L. P. Dron,<br>L. S. Kejser, I. P. Nesterova, and P. I. Patrashku,<br>All-Union Institute for Biological Methods of Plant<br>Protection    |     |

# CONTENTS (continued)

|                                                                                                                                    |     |
|------------------------------------------------------------------------------------------------------------------------------------|-----|
| Studies of the Behavior of Organophosphorous Insecticides<br>in Soil and in Soil-Plant System . . . . .                            | 151 |
| T. M. Petrova, K. V. Novozhilov, T. A. Evstigneyeva,<br>and F. I. Kopytova, All-Union Research Plant Protection<br>Institute       |     |
| Pesticide Transport and Transformation in Animals<br>Co-Chairmen: J. E. Casida (USA) and Y. S. Kagan (USSR)                        |     |
| Metabolism of Pyrethroid Insecticides and Thiocarbamate<br>Herbicides . . . . .                                                    | 163 |
| J. E. Casida, University of California                                                                                             |     |
| Basic Trends and Results in the Study of Pesticide Toxicology . . .                                                                | 171 |
| Y. S. Kagan, USSR Ministry of Public Health                                                                                        |     |
| Metabolism and Persistence of Pesticides and Other Xenobiotic<br>Chemicals in Fish. . . . .                                        | 187 |
| J. J. Lech, Medical College of Wisconsin                                                                                           |     |
| Pesticide Movement in the Organism of Farm Animals. . . . .                                                                        | 190 |
| G. A. Talanov, Research Institute of Veterinary Sanitation                                                                         |     |
| Mathematical Modeling of Pesticide Transport and Transformation<br>Co-Chairmen: D. W. Duttweiler (USA) and V. M. Voloshchuk (USSR) |     |
| Mathematical Modeling of Pesticides in the Environment. . . . .                                                                    | 194 |
| J. Hill, IV, U. S. Environmental Protection Agency                                                                                 |     |
| Quality Analysis and Numerical Experiment in Analyzing the<br>Effect of the Anthropogenic Pollution of the Biota . . . . .         | 198 |
| V. M. Voloshchuk, Institute of Experimental Meteorology                                                                            |     |
| Basic Mathematical Models of Toxicant Transport through<br>the Soil Profile . . . . .                                              | 201 |
| V. V. Rachinskii, Timiryazev' Academy of Agricultural<br>Sciences                                                                  |     |
| Mathematical Modeling and Control as a Radical Way of<br>Environmental Protection from Pesticide Contamination. . . . .            | 210 |
| E. I. Spynu, USSR Ministry of Public Health                                                                                        |     |
| Modeling of Pesticide Degradation in Plants and Evaluation<br>of Their Application Systems . . . . .                               | 223 |
| L. N. Ivanova, USSR Ministry of Public Health                                                                                      |     |
| The Model of the Pesticide Circulation in Fergana Valley. . . . .                                                                  | 230 |
| V. M. Koropalov and I. M. Nazarov, Institute of Applied<br>Geophysics                                                              |     |



## INTRODUCTION

As part of the 1972 USA-USSR Agreement on Cooperation in the Field of Environmental Protection, a cooperative program of information exchange on the environmental transport of agricultural chemicals (pesticides and fertilizers) began in 1974. Scientists from both countries visited major research centers to become familiar with the use of pesticides and nutrients in agriculture and with current concepts and research on environmental effects of these chemicals.

To focus on a scientific question of particular mutual concern, the joint project committee sponsored a 7-day symposium on the Environmental Transport and Transformation of Pesticides, which was hosted by the Soviet side at Tbilisi on 20-27 October 1976. The symposium was held in conjunction with the fourth meeting of the USA-USSR Joint Project Committee for Project 02.03-31, "Forms and Mechanisms by Which Pesticides and Chemicals are Transported." Eleven US delegates met with 26 Soviet scientists to discuss six main topics: pesticide transport and transformation in the atmosphere in soil, in water, in plants, and in animals, and mathematical modeling techniques for characterizing pesticide migration and transformation in the environment. Opening remarks by G. G. Svanidze (USSR), D. W. Duttweiler (USA), and S. G. Malakhov (USSR) emphasized mutual interest in the symposium topic; the importance of pesticides to agricultural productivity; and the value of scientific understanding of the environmental entry, transport, transformation, ecological effects, and ultimate residual distribution of pesticides.

This document is a compilation of extended abstracts of papers presented at the symposium. English translations of the Soviet papers were provided by the USSR and have not been altered. A brief summary of the symposium appeared in the Journal of Agricultural and Food Chemistry, Volume 25, Number 5, pp. 975-978, September/October 1977.

## ATMOSPHERIC TRANSPORT AND TRANSFORMATION OF PESTICIDES

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Pesticides enter the atmosphere on dust particles and by volatilization from soil and water surfaces, and thus they can travel over great distances. Cohen and Pinkerton (1) traced the 2000 km movement of a dust cloud from an agricultural area in Western Texas to Cincinnati, Ohio (Fig. 1), where DDT, DDE, and 5 other pesticides were detected in it. Rain falling on Ohio also contained these and other pesticides (Table I).

Many pesticides are quite volatile under certain conditions (2). Although the vapor pressure of DDT is only  $7.2 \times 10^{-7}$  torr (30°C), it evaporates from treated fields at a rate of 5-10 kg/ha/yr (3), depending upon temperature, moisture, and air movement. However, DDT derivatives such as o,p'-DDT, DDD, and DDE are more volatile than DDT itself and also are found after DDT application due to their presence in formulations or to biological and nonbiological breakdown. Consequently, 66% of the total DDT atmosphere over a treated field was DDE, and most of the DDT in aerated soil probably will be volatilized eventually as DDE (Table II). Accurate measurements of vapor pressures are important in predicting volatilization rates but are available to only a very limited extent (4).

Mackay and co-workers (5,6) have calculated the residence time of several pesticides and other chemicals in water in relation to vapor pressure, concentration, and other measurable properties (Table III) and have corrected the values for mass transfer rate. The results indicate much faster transfer of pesticides from water into the atmosphere than had been generally recognized; for example, the corrected half-life of DDT in water of 1 m depth is calculated to be 73.9 hrs. Such values are consistent with experimental observations (3).

Due largely to this volatilization, pesticides have been detected in the atmosphere over both urban and agricultural areas of the United States. Stanley and co-workers (7) collected air samples at 9 locations and analyzed them for 18 compounds (Fig. 2). DDT and related substances always were present, BHC isomers tended to occur over urban areas, but campheclor (toxaphene) and parathion were found only in rural locations. High levels often corresponded to periods of low rainfall. Apparently, loss to the atmosphere either as vapor or particulate matter represents a major aspect of pesticide transport.

The presence of light, water, reactive surfaces, oxygen, and other oxidants are thought to cause pesticide transformations in the atmosphere. Many pesticides undergo photochemical decomposition in water or other solvents (8), and similar breakdown in the vapor state is not surprising. For example, irradiation of the herbicide trifluralin (I) in vapor form with ultraviolet light (wavelengths greater than 290 nm) in a glass reactor (9) rapidly provided the dealkylated and cyclicized products (Fig. 3) reported earlier from irradiation of solutions (10,11). DDE vapor reacted similarly to form DDMU, 4,4'-dichlorobenzophenone (VI), a DDE isomer (VII), and chlorinated biphenyls (12) (Fig. 4).

In order to confirm that the same reactions actually take place in the atmosphere above treated fields, high-volume air samplers were constructed either of glass (Fig. 5A) or metal (Fig. 5B). Atmospheric constituents were caught by glass-fiber filters or by solid, unreactive adsorbents and could be collected at rates exceeding one m<sup>3</sup>/min. The air over fields treated with technical trifluralin -- on the soil surface, incorporated into the soil, or released directly into the atmosphere as vapor -- was shown to contain the expected photodecomposition products (11) (Fig. 6). Note in the figure that photoproduct formation must have been very rapid initially.

A similar comparison of laboratory and field data for the insecticide parathion (VIII) (13,14) (Fig. 7) showed that atmospheric oxidants and solid surfaces were important for photochemical changes; parathion vapor in an orchard was converted to paraoxon (IX) and then to p-nitrophenol which represented a stable end-product.

Although only very limited data have appeared on this subject, the existing evidence shows clearly that many pesticides can be expected to move readily from soil, water, and other surfaces into the atmosphere and then be transformed by abiotic chemical reactions into the rather stable and sometimes unexpected products (for example, the chlorinated biphenyls, nitrobenzimidazoles, and p-nitrophenol mentioned here).

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Table I. Pesticides Precipitated from the Atmosphere at Cincinnati, Ohio (1)

|           | Pesticide Content |                     |
|-----------|-------------------|---------------------|
|           | Dust (ng/g)       | Rain (ng/ml)        |
| DDT       | 600               | 0.34 (0.07 - 1.30)  |
| DDE       | 200               | 0.02 (0.005 - 0.02) |
| Chlordane | 500               | +                   |
| 2,4,5-T   | 40                | +                   |
| Dieldrin  | 3                 | +                   |

+ Signifies detected but not measured

Table II. Volatilization of Pesticides from DDT-Treated Soil (3)

| Chemical | In Soil         |                   | In Atmosphere   |                   |
|----------|-----------------|-------------------|-----------------|-------------------|
|          | $\mu\text{g/g}$ | Ratio to p,p'-DDT | $\text{ng/m}^3$ | Ratio to p,p'-DDT |
| p,p'-DDT | 14.1            | 1.0               | 104             | 1.0               |
| p,p'-DDE | 6.2             | 0.44              | 419             | 4.03              |
| o,p'-DDT | 2.7             | 0.19              | 69              | 0.66              |
| o,p'-DDE | 0.12            | 0.008             | 26              | 0.25              |
| Total    | 23.1            | ...               | 618             | ...               |



Table III. Calculated Evaporation Rates at 25°C (5)

|               | Solubility<br>(mg/l) | Vapor Press<br>(Torr) | T <sub>1/2</sub><br>(hrs) |
|---------------|----------------------|-----------------------|---------------------------|
| Biphenyl      | 7.48                 | 0.057                 | 7.5                       |
| Arochlor 1254 | 0.012                | $7.7 \times 10^{-5}$  | 10.3                      |
| DDT           | 0.001                | $1 \times 10^{-7}$    | 73.9                      |
| Aldrin        | 0.2                  | $6 \times 10^{-6}$    | 185                       |
| Lindane       | 7.3                  | $9 \times 10^{-6}$    | 4,590                     |
| Dieldrin      | 0.25                 | $1 \times 10^{-7}$    | 12,940                    |

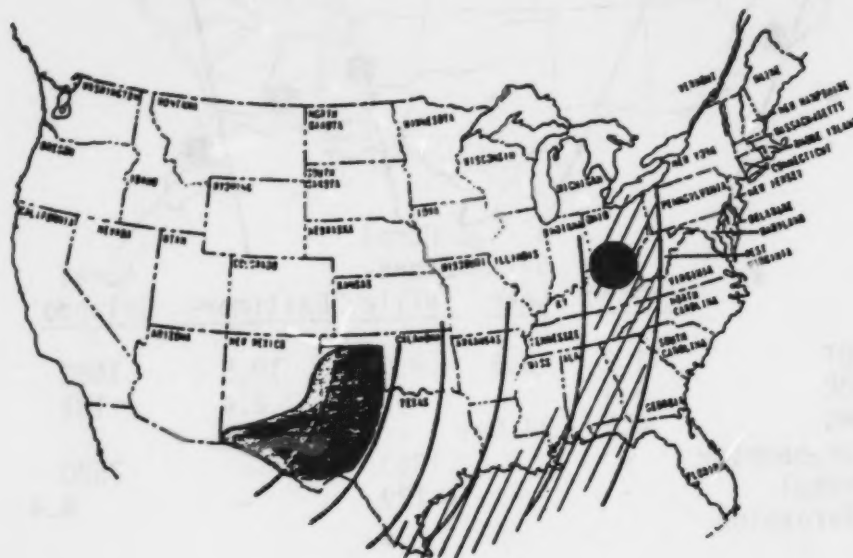


Fig. 1. Pesticide movement on dust from Texas to Ohio, January 1964 (1).  
Each curved line indicates 6 hours.

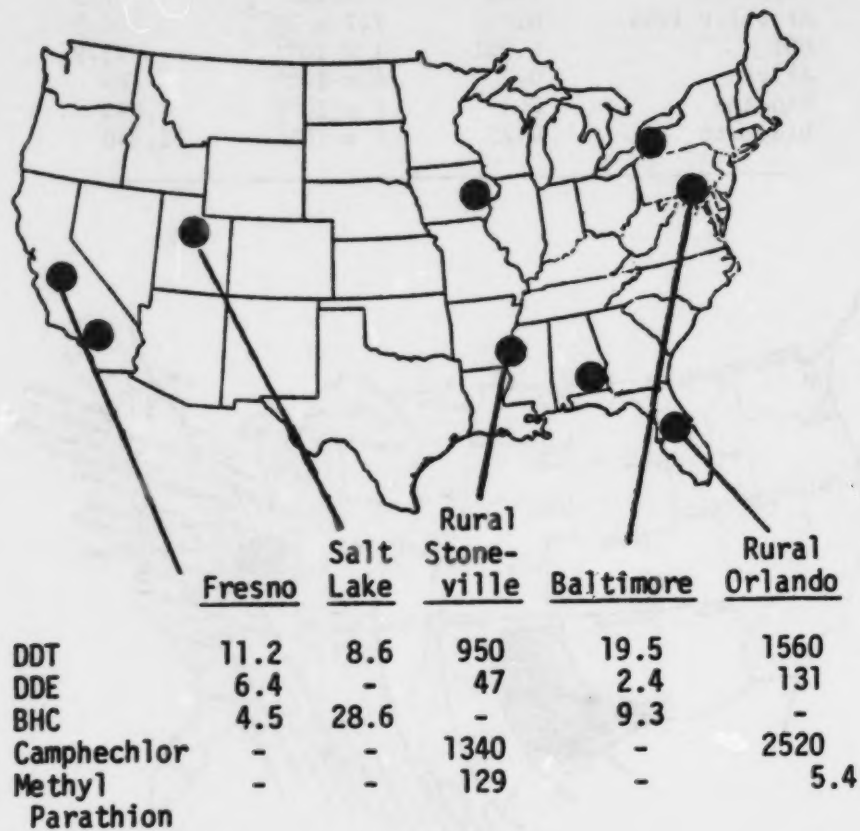


Fig. 2. Pesticides in the lower atmosphere ( $\text{ng/m}^3$ ) at 5 U.S. Sites in 1970 (7).

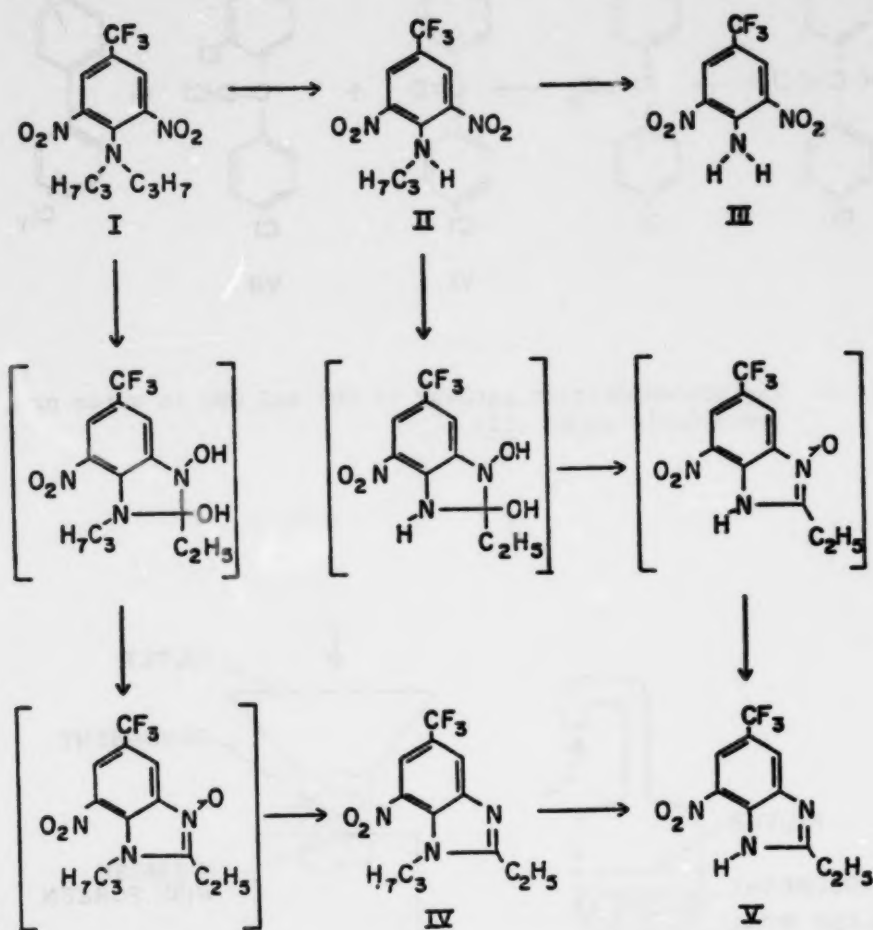


Fig. 3. Photodecomposition pathway of trifluralin (I) in water or as atmospheric vapor (10,11).

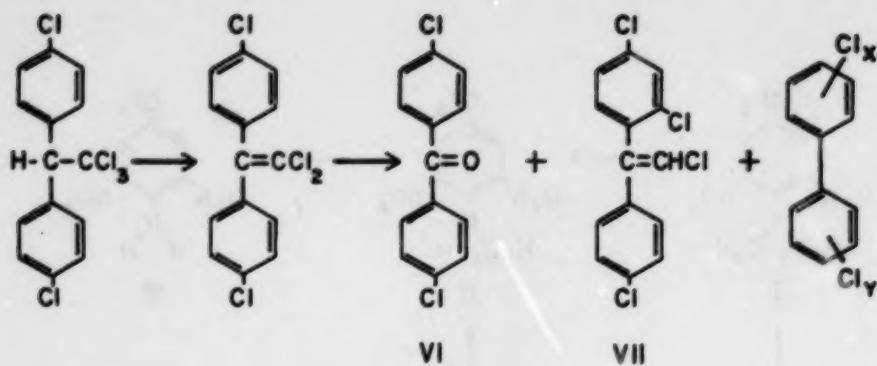


Fig. 4. Photodecomposition pathway of DDT and DDE in water or as atmospheric vapor (12).

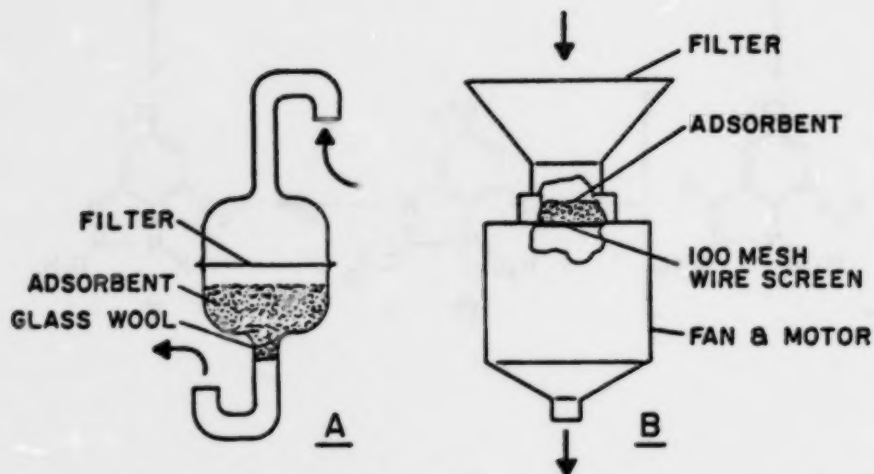


Fig. 5. Diagrams of high-volume air samplers made of glass (A) or metal (B) (11).

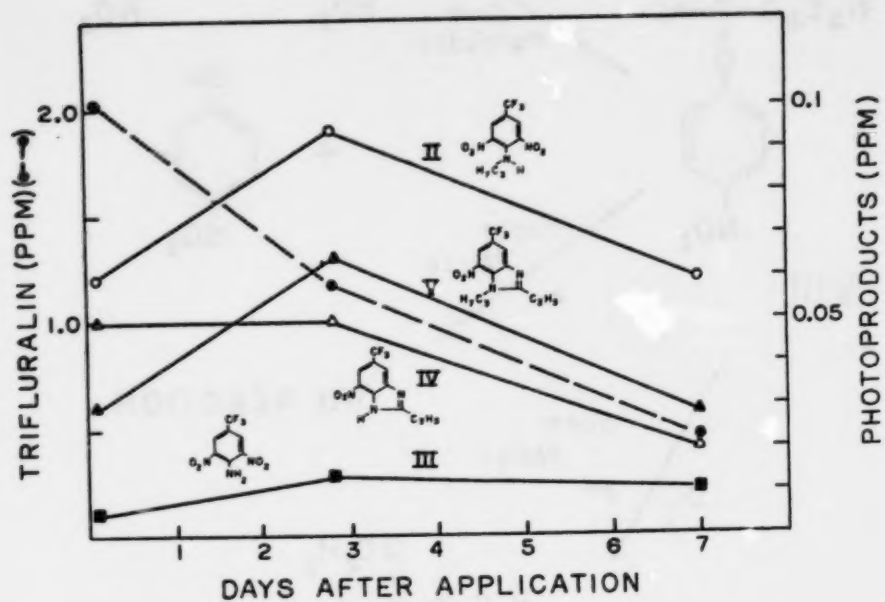


Fig. 6. Recovery of trifluralin and its major photodecomposition products from the atmosphere by high-volume air sampling (11).



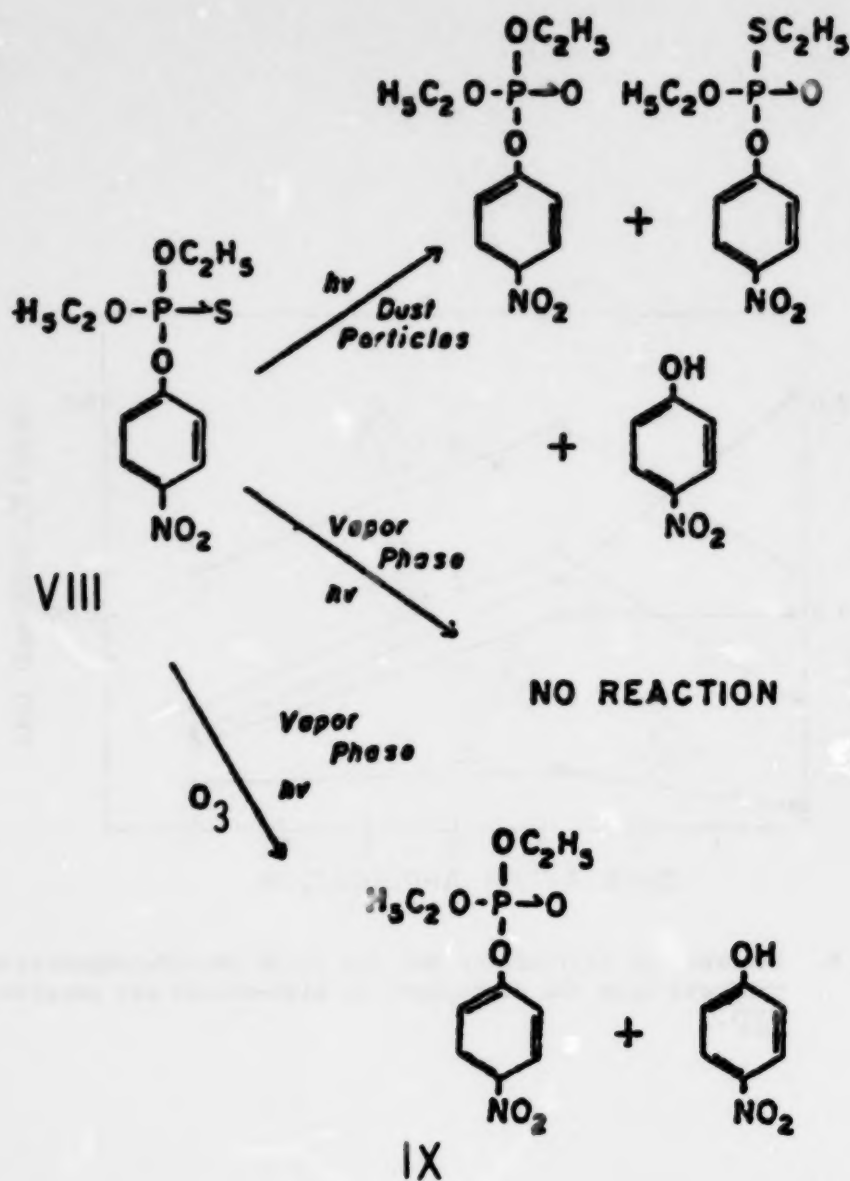


Fig. 7. Photodecomposition of parathion (VIII) vapor alone or in the presence of ozone or dust particles (13,14).

## ATMOSPHERIC TRANSPORT OF DDT

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When studying pesticide transport, in particular, DDT transport, we have to deal with phenomena of various scales. First, it is pesticide dissipation at the instant of application. It corresponds to the smallest scales, that is, the maximum transport is several kilometers from the application site. Small height of application and rough dispersity may be responsible for it. Second, it is pesticide transport on soil particles at wind erosion. Corresponding regional scales may be as great as hundreds and sometimes thousands kilometers. An increase in scales is related to the height of dust cloud lifting. An increase in the scale of transport of the particles not completely carried with turbulent air pulsations was estimated to be proportional to the cloud height over the underlying surface, and that of the completely carried particles - proportional to the square of the height. From this it is not difficult to obtain the above-mentioned difference in scales. However, these estimates are valid for sufficiently large particles which are completely absorbed by the underlying

surface. For small particles of about 1 to 5 microns and pesticide vapors which are poorly absorbed by the underlying surface the scales of transport substantially vary, and conditions are created to draw pesticides into the global transport. It is the maximum scale of the process.

Let us briefly dwell on the advances and problems of investigations in the levels of air pollution and transport processes for each scale.

1. Near zone. It has received the most study. Dependences have been found of the concentrations and transport on the size of aerosols, method of application, pesticide volatility, meteorological conditions [1-5]. Problems occurred are the following: variability of the results under different patterns of the underlying surface (arable land, grass, forest) and lack of the appropriate regularities.

2. Regional scale. Results of the pesticide concentration measurements over the territory of the United States are given in [6] which show substantial variability with time (the p,p'-DDT concentrations varied from 0.1 to 1500 ngr/m<sup>3</sup>). Higher levels were observed in the neighbourhood of rural areas at the instances which most of all favoured evaporation or occurrence of the dense dust conditions. In the latter case the most part of the total amount of DDT found in the samples was on dust particles. These problems were also discussed in [7] where pesticide concentrations in the atmospheric dust in Cincinnati (Ohio) were given. It has been found that the DDT concentration varied from 3 to 90 ppm. From the total amount of fallen dust it has been estimated that every month from 45 to 270 g of DDT per km<sup>2</sup>

fell on the ground. Air pollution with pesticides in the regional scale was also studied in the Soviet Union using as an example DDT in Fergana valley and Khorezm oasis in Central Asia. Fergana valley is a vast inter—mountain hollow with the intensive aeration from December to April. Over the other periods the aeration conditions substantially deteriorate. Stagnant phenomena are rather widespread and can lead to the greater pollution of the whole air volume of the valley with pesticides. In addition to this, large areas in the valley are affected by strong wind erosion and there occur dust storms. Results of the vertical profile measurements of DDT, DDD, and DDE concentrations over the periods of slight winds (experiments No. 1, 2, 3) and strong dust storm (4) are given in Table I.

In the former case  $10^2$  kg of DDT was contained in the air volume in the valley whereas in the latter one  $10^3$  kg was found. Experiment No. 5 was carried out in Khorezm oasis where stagnant phenomena were absent. In the latter case the amount of pesticides transported from the area on aerosol particles was evaluated at about  $10^2$  kg. All the profiles given in Table I may be described by the following formula [8] :

$$C(z) = C(h) \exp \left[ - \frac{\bar{v}}{K} (z - h) \right] \quad (I)$$

where  $C(h)$  is the concentration at the upper boundary of the surface layer;

$K$  is the coefficient of turbulent diffusion;

$\bar{v}$  is the average rate of particle deposition.

Table I. Pesticide concentrations (DDT, DDE, DDD) on aerosol particles in Fergana valley (experiments No. I-4) and Khorezm oasis (experiment No. 5)

| No. of experiment | Height of sampling : (m) | Concentrations x 10 <sup>-10</sup> g/m <sup>3</sup>     |    |   |     |
|-------------------|--------------------------|---------------------------------------------------------|----|---|-----|
|                   |                          | : p,p'-DDT: p,p'-DDD + o,p'-DDT: p,p'-DDE: $\Sigma$ DDT |    |   |     |
| I                 | 50                       | 120                                                     | 24 | - | 144 |
|                   | 100                      | 94                                                      | 17 | - | 111 |
|                   | 200                      | 70                                                      | 10 | - | 80  |
|                   | 300                      | 83                                                      | 13 | - | 96  |
|                   | 400                      | 41                                                      | 4  | - | 45  |
|                   | 600                      | 20                                                      | 2  | - | 22  |
|                   | 800                      | 17                                                      | 4  | - | 21  |
|                   | 1000                     | 15                                                      | 5  | - | 20  |
|                   | 1200                     | 15                                                      | 3  | - | 18  |
|                   | 1800                     | 3                                                       | 1  | - | 4   |
|                   | 2500                     | 4                                                       | 2  | - | 6   |
| 2                 | 100                      | 270                                                     | 30 | - | 300 |
|                   | 200                      | 190                                                     | 10 | - | 200 |
|                   | 300                      | 140                                                     | 20 | - | 160 |
|                   | 400                      | 140                                                     | 10 | - | 150 |
|                   | 600                      | 68                                                      | 8  | - | 76  |
|                   | 800                      | 48                                                      | 5  | - | 53  |
|                   | 1000                     | 40                                                      | 6  | - | 46  |
|                   | 1200                     | 28                                                      | 5  | - | 33  |
|                   | 1800                     | 36                                                      | 3  | - | 39  |
|                   | 2500                     | 6                                                       | 2  | - | 8   |



|   |      |     |     |    |     |
|---|------|-----|-----|----|-----|
| 3 | 200  | 66  | 18  | 8  | 92  |
|   | 300  | 42  | 13  | 4  | 59  |
|   | 500  | 34  | 10  | 5  | 49  |
|   | 1000 | 7   | 4   | 2  | 13  |
|   | 1500 | 12  | 4   | 3  | 19  |
|   | 2000 | 8   | 3   | 4  | 15  |
| 4 | 50   | 400 | 60  | 30 | 490 |
|   | 100  | 420 | 70  | 25 | 515 |
|   | 200  | 550 | 110 | 57 | 717 |
|   | 400  | 500 | 75  | 30 | 605 |
|   | 600  | 250 | 45  | 24 | 319 |
|   | 900  | 170 | 25  | 24 | 219 |
| 5 | 50   | 28  | -   | -  | 28  |
|   | 100  | 45  | 10  | 10 | 65  |
|   | 200  | 41  | 15  | 11 | 67  |
|   | 400  | 88  | 21  | 10 | 79  |
|   | 500  | 24  | 10  | 8  | 42  |
|   | 1000 | 13  | 5   | 8  | 26  |

Knowing  $K$  which in experiments No. 1, 2, 3, 5 was about  $5 \text{ m}^2/\text{sec.}$ , it is not difficult to find that the average rate of DDT deposition is approximately  $1 \text{ cm/sec.}$  This gives from 100 to 500 g of DDT per  $\text{km}^2$  during a month that agrees with the data obtained by the American authors. However, these estimates can not be made until the bulk of pesticide is absorbed on large aerosol particles. If a pesticide is on the particles of about 1 to 5 microns or in vapor phase this impurity behaves as weightless, and the mentioned distribution with height should not occur. This

means that we can not say definitely about depositions from the measurements of concentration profiles. Their direct measurement is required. This problem is to be faced when determining depositions at some distance from the rural region where a rough-dispersive fraction of aerosol particles is already absent. Pesticide strikes the ground either due washing-out or through dry deposition of weightless impurity. There is a progress in the studies of washing-out after the work [8] where the coefficients of washing-out were found for the vapor phase of lindane, dieldrin, and DDT. It is worse with the dry deposition of small aerosol particles or with the adsorption of pesticide vapors. Available are only the data [9] on the rate of DDT vapor deposition on water and glass surfaces ( $5 \times 10^{-2}$  cm/sec. and  $4 \times 10^{-4}$  cm/sec., respectively). Under actual conditions these data for aerosol and vapor components have not been obtained. Not numerous works [10, 11] showed that the rate of deposition  $\mathcal{L}$  depends on the pattern of the underlying surface, the value of particle cohesion with the surface, etc. However, it has not been possible to obtain any regularities other than the dependence on the dynamic wind velocity  $v^*$ :

$$\mathcal{L} = \alpha v^* \quad (2)$$

The flow on the underlying surface ( $\mathcal{L} = 0$ ) turned out to be related to  $\alpha$  in the following way:

$$j = \mathcal{L}C \Big|_{z=0} = \alpha v^* C \Big|_{z=0} \quad (3)$$

However, all information on the surface properties is given as before by a single parameter  $\alpha$ . We made an attempt to find an explicit dependence of  $\mathcal{L}$  on the underlying surface parameters being measured

[I2]. For this purpose the surface was represented by the layer of vegetation with the height  $\mathcal{L}$  and specific surface  $S$ . Consideration was given to the impurity diffusion in this layer and deposition on the surface of vegetation and soil. For  $\mathcal{L}$  the following expression has been obtained:

$$\mathcal{L} = \sqrt{\alpha S \lambda v^* \mathcal{L}_p} \left( 1 - \frac{2}{1 + \frac{1+\beta}{1-\beta} e^{\frac{2\mathcal{L}}{\mathcal{L}_0}}} \right) \quad (4)$$

where  $\beta = \mathcal{L}_s (\alpha S \lambda v^* \mathcal{L}_p)^{-\frac{1}{2}}$ ,  $\mathcal{L}_0 = (\alpha \lambda v^* / S \mathcal{L}_p)^{\frac{1}{2}}$ ,  $\mathcal{L}_p$  and  $\mathcal{L}_s$  coincide with  $\mathcal{L}$  in physical meaning for the plain surfaces having the properties of vegetation and soil, respectively;

$\alpha$  is the universal constant;

$\lambda$  is the characteristic scale within vegetation.

The dependence on dynamic velocity turned out to be more complex than (2). The latter occurs only under the fulfilment of the following condition:

$$\mathcal{L}_s \ll \frac{\alpha \lambda v^*}{\mathcal{L}} \quad (5)$$

We believe that the obtained dependences of deposition rate on the underlying surface parameters will aid in arrangement of the appropriate experiments. In the end this will provide opportunities to find the portion of pesticides deposited on the ground from a given source and drawn into the global transport. In particular, knowing  $\dot{j}$ , it is possible to predict the regional pesticide transport. Prediction scheme can be reduced to solution of the turbulent diffusion equation with the appropriate transport coefficients and boundary condi-

tions. The major problem here is selection of the scales of averaging. Both diffusion coefficients and the rates and directions of average transport will change depending on this. We performed calculations of the amount of DDT depositions on the ground from Khorezm oasis which agree qualitatively with the measured ones.

3. Global scale. Analysis of the data on the global levels of atmospheric pollution with persistent pesticides shows that these levels are very variable and substantially depend on synoptic conditions and air currents in the lower troposphere. According to the data obtained by the American authors which relate mainly to the Atlantic ocean, the levels of DDT concentrations vary from  $20 \times 10^{-12} \text{ g/m}^3$  [13] to  $200 \times 10^{-12} \text{ g/m}^3$  [14]. These levels were found on aerosol component. As regards the pesticide content in vapor phase, there is no agreement on this problem for lack of reliable techniques of separation of aerosol and vapor components.

It was shown in work [15] that the toxaphene concentrations over the Atlantic ocean in the area between the Bermudas and the U.S. sea coast are due to the transport of this pesticide from the southern states of the United States. Therefore the maximum concentrations were observed in these areas when there occurred the air masses of appropriate origin. From this it follows that it is essential to know about the air mass history when studying fluctuations of the global levels of atmospheric pollution. We should like to place emphasis on the fact that neglect of these factors can lead to wrong interpretation of the experimental data. <sup>PM</sup> Prospero and <sup>SB</sup> Saba [14] report on several cases of high and low values of DDT concentrations nearby Barbados and compare these concentrations of pesticide and those of dust. Thus, on July 16,



1970 high DDT concentrations and Low those of dust were observed, whereas on July 18, 1970, on the contrary, DDT concentrations were low and those of dust were high. For reasons given it was concluded in this work that the Sahara dust had a washing effect on pesticides over the aquatoria of the Atlantic ocean. However, a detailed analysis of meteorological situations showed that high pesticide concentration levels occurred at the instants of air mass advection from the territory of the American continent. Low concentrations were related to the air mass transport with trade winds from the Sahara. It should be noted that the values of the background level of pesticide concentrations serve as the basis for the development of corresponding balance models and pesticide global circulation models. Taking into consideration scant statistics of the background measurements and their high variability, we should impose heavy demands on their interpretation.



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## DISPARLURE AND SOME JUVENILE HORMONE ANALOGUE

### PERSISTENCE IN THE ENVIRONMENT

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Necessity of the working out of new principles of plant protection from harmful insects, that provide purity of the environment, has led to the investigations on pesticides of the third generation - attractants and juvenile hormone analogues. A rather voluminous material on their field and production tests has been accumulated. Much less is known on their stability and persistence in the environment though these problems have to be solved as well.

Attractant effectiveness depends on a number of factors among which the presence of pheromone vapours in the air seems to be the main one. Their release rate into <sup>the</sup> atmosphere is almost not studied. Practically there are data on vapour pressure and some compounds volatility. There are no such data on disparlure - cis-7,8 epoxymethyloctadecane - gypsy moth attractant as well.

To get these data we used the classical method such as pure dry air blowing over disparlure surface. The air was dried and absorbed by passing through calcium chloride and activated carbon

AG-3. Vapour catching took place in two successively connected traps filled with hexane and plunged into the cooling mixture. The vessel with disparlure was put into the thermostat. Disparlure was determined with the help of gaschromatography. The results are given in Table I. Pressure curve of disparlure vapour and volatility curve calculated according to the least square method are of linear character and correspond to the equations

$$\log P = - 5,2757 + 0,02216$$

$$\log F = - 1,4248 + 0,02973$$

These data gave possibility to approach a question of disparlure determination in air. At present, works on disparlure identification in the air, its environmental metabolism are carried

Table I.

Vapour pressure and volatility of disparlure at different temperatures

| Temperature,<br>°C | : Vapour pressure, mm Hg :<br>column x 10 <sup>-5</sup> | Volatility,<br>μg/l |
|--------------------|---------------------------------------------------------|---------------------|
| 15                 | 1,03                                                    | 0,09                |
| 20                 | 1,38                                                    | 0,13                |
| 25                 | 1,81                                                    | 0,20                |
| 30                 | 2,43                                                    | 0,29                |
| 35                 | 3,18                                                    | 0,42                |
| 40                 | 4,12                                                    | 0,60                |
| 45                 | 5,20                                                    | 0,86                |
| 50                 | 6,76                                                    | 1,21                |

out in the laboratory. The results will be published. At controlled temperature (20-35°C) and relative air humidity (40-50% and 80-100%) conditions volatilization rate of disparlure applied on foil plates was investigated. Disparlure residue was determined with the help of gaschromatography. Obtained data, being statistically processed, showed significant influence of temperature and air movement on this process (Fig.I). The importance of humidity influence on the process of disparlure release wasn't proved.

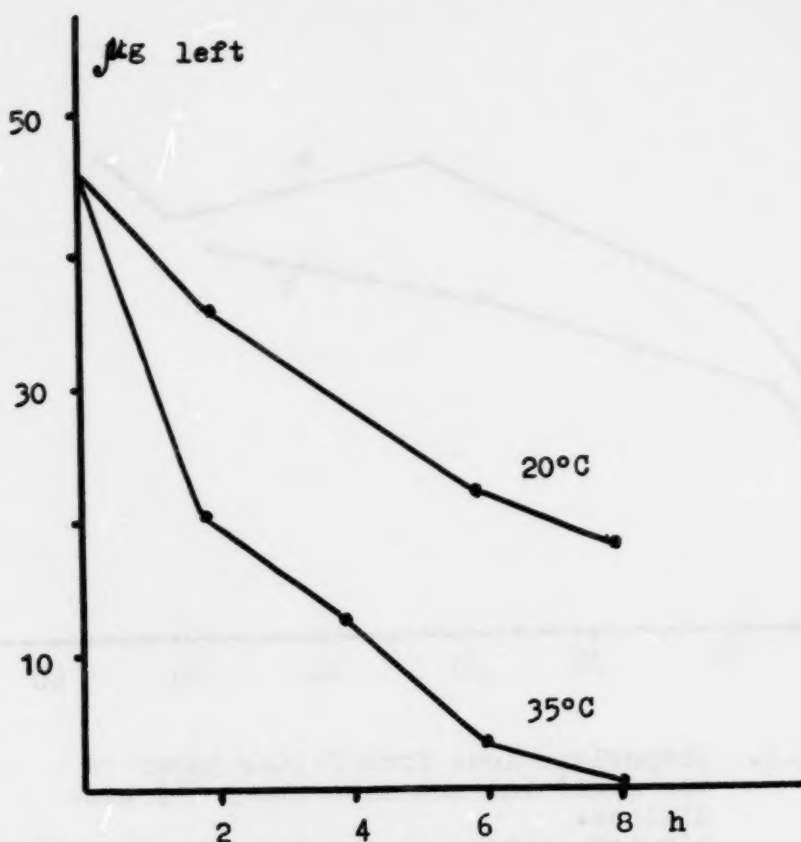


Figure I. Temperature influence on loss of disparlure from the foil plates.

Obtained data on the release of disparlure applied on filter paper in laboratory and field tests correlate well (Fig.2).

The results show that disparlure evaporates quickly and it gives possibility to think that it will be absorbed by soil and water.

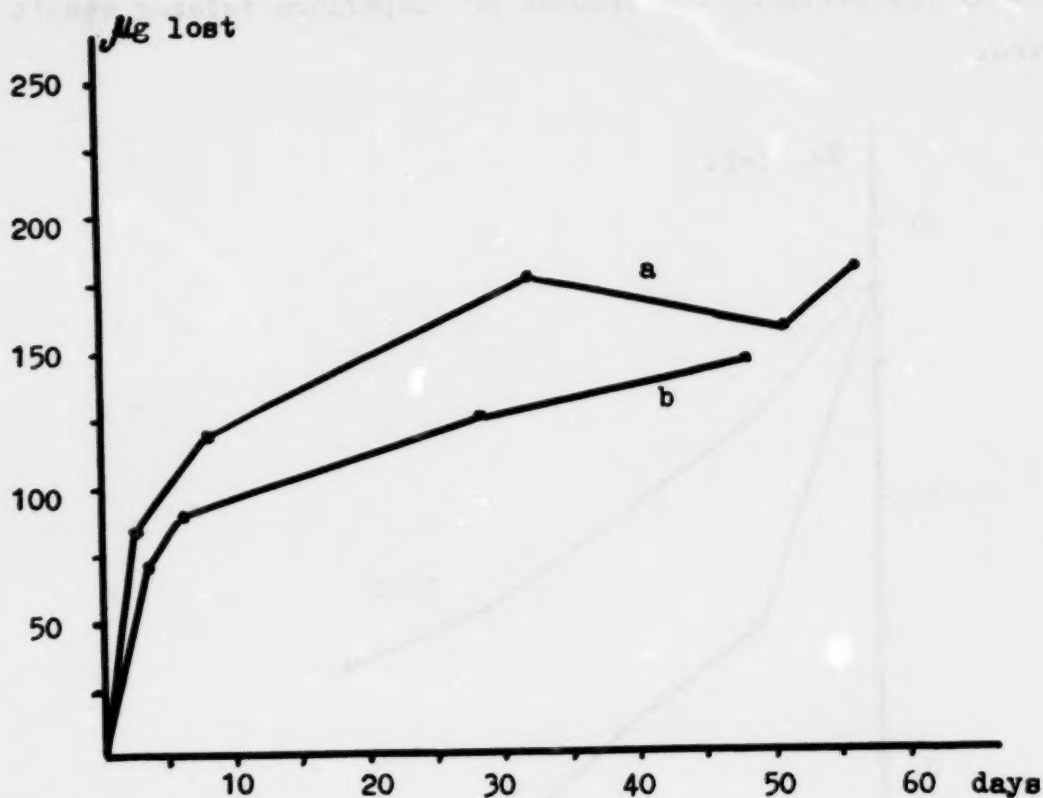


Fig.2. Disparlure loss from filter paper in the field (a) and laboratory (b) conditions. Air temperature in the field is 20 -25°C, in thermostate - 25°C; wind speed in the field is 1,0-2,1 m/sec., in thermostate - 1,5 m/sec.



Juvenile hormone analogues as plant protection means from noxious insects are used the same way as classical pesticides. Applied compounds can volatilize, influenced by sun, temperature, oxygen, air humidity, wind and other factors, that in the end can lead to the possibility of the environmental pollution. Investigations that had been carried out on some juvenile hormone analogues: altosar (ethyl-3,7,II-trimethyl-dodeca-2,4-dienoate), altosid (isopropyl-II-methoxy-3,7,II-trimethyl-2,4-dodecadienoate) and bromphenoxygeraniol /I-(4-B-phenoxy)-3,7-dimethyl-2,6-octadiene/ - allowed to determine interrelation between vapour pressure and altosar, altosid and bromphenoxygeraniol volatility and their persistence time on treated surface (Table 2). Rather high vapour pressure and altosar and altosid volatility lead to a high rate of technical product loss in the process of air blowing. At the same time bromphenoxygeraniol is not enough volatile and it may be expected that it will persist longer in field conditions. Light can also cause degradation of these compounds. In our experiments short time ultra-violet irradiation of bromphenoxygeraniol (about 1 hour) leads to its practically complete degradation. Polar zone formation was identified by thinlayer chromatography.

Sunlight irradiation of bromphenoxygeraniol gives analogous results but the process is retarded. In 18 hours 20,9% of the compound in comparison with the initial amount was found on treated surface. The study of temperature influence on bromphenoxygeraniol showed that in closed volume it was stable in the range 30-80°C (Fig.3). At temperatures higher than 80°C a significant decrease in

Table 2

Vapour pressure, volatility and persistence of  
some juvenile hormone analogues on potatoes

| Compound                 | : °C | : P mm<br>Hg column   | : Vo-<br>la-<br>ti-<br>li-<br>ty,<br>mg/<br>:m <sup>3</sup> | : Persistence, µg/g<br>leaves | time (days)                     |       |        |                                  |     |
|--------------------------|------|-----------------------|-------------------------------------------------------------|-------------------------------|---------------------------------|-------|--------|----------------------------------|-----|
|                          |      |                       |                                                             |                               | : Ini-<br>tial<br>: amo-<br>unt | : I   | : 2    | : 3                              | : 4 |
| Altosar                  | 20   | 6,04.10 <sup>-4</sup> | 8,87                                                        | 0,26                          | 0,094                           | 0,016 | traces | not<br>de-<br>tec-<br>ted        |     |
| Altosid                  | 20   | 5,25.10 <sup>-3</sup> | 91,75                                                       | 0,62                          | 0,430                           | 0,048 | 0,024  | 0,005                            |     |
| Bromphenoxy-<br>geraniol | -    | not deter-<br>mined   | -                                                           | 59,0                          | 7,45                            | -     | 4,08   | not<br>de-<br>ter-<br>mi-<br>ned |     |

the compound content was noticed. In field conditions wind is another factor that decrease bromphenoxygeraniol content. As a result of the influence of all studied factors in laboratory and field tests on potato plants treated with emulsifiable concentrates of altosar (53% a.i. ), altosid (65,5% a.i.) and bromphenoxygeraniol (100%) at rates 1,5 and 3 kg per hectare, persistence time of juvenile hormone analogues on leaves was not more than 3-5 days (Table 3). When rainfall occurs persistence time of altosar and altosid was sharply reduced. Thus under the influence of heavy

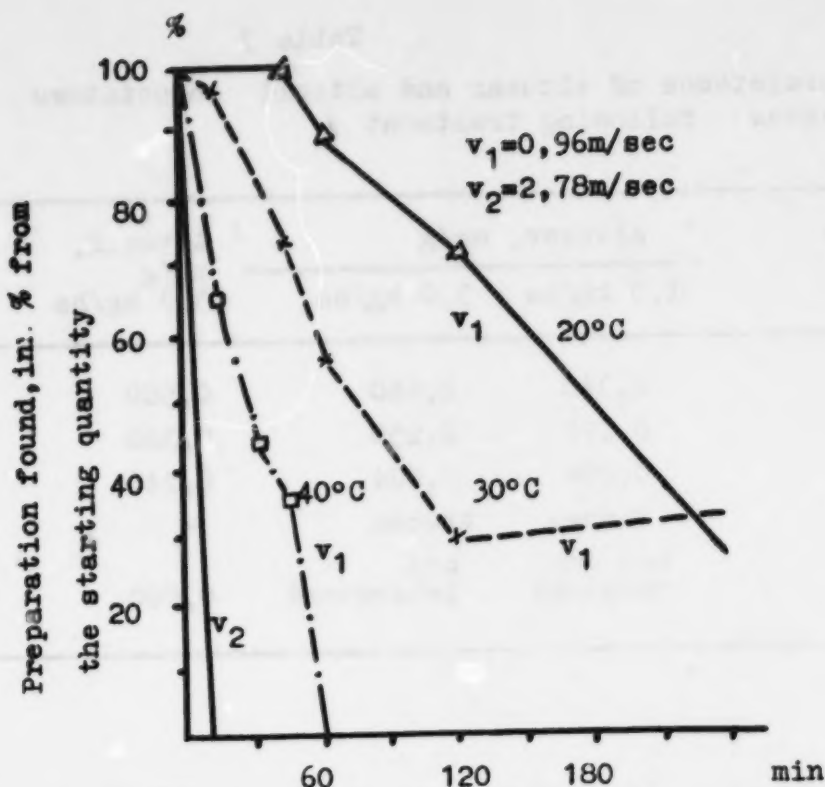


Figure 3. Bromphenoxygeraniol loss from the glass surface as influenced by temperature and wind.

showers in 24 hours only altozar traces were found on potato leaves. Altosid persisted a little bit longer. In 24 hours about 50% of the compound was found, in 48 hours - 6,5% as compared with the initial amount.

The study of persistence time of juvenile hormone analogues in soil is also of significant interest. In the laboratory test the influence of these factors on altosid persistence time in the soil was studied under controlled temperature and soil humidity conditions. Investigations showed (Fig.4) that altosid degrades

Table 3

Persistence of altozar and altosid on potatoes  
leaves following treatment

| Time, days | : Altozar, mg/g       |                   | : Altosid,        |
|------------|-----------------------|-------------------|-------------------|
|            | I,5 kg/ha : 3,0 kg/ha |                   | mg/g<br>3,0 kg/ha |
| 0          | 0,340                 | 0,650             | 0,500             |
| 1          | 0,170                 | 0,250             | 0,380             |
| 2          | 0,004                 | 0,004             | 0,240             |
| 3          | traces                | traces            | -                 |
| 8          | not de-<br>termined   | not<br>determined | 0,060             |

quickly in the soil. Its losses were in average 98,6% at 20°C in 14 days after treatment. The increase of temperature to 30°C reduces persistence time to 10 days, the increase to 40°C - to 4-6 days. The increase of relative soil humidity from 18% to 30% accelerates altosid degradation in the soil.

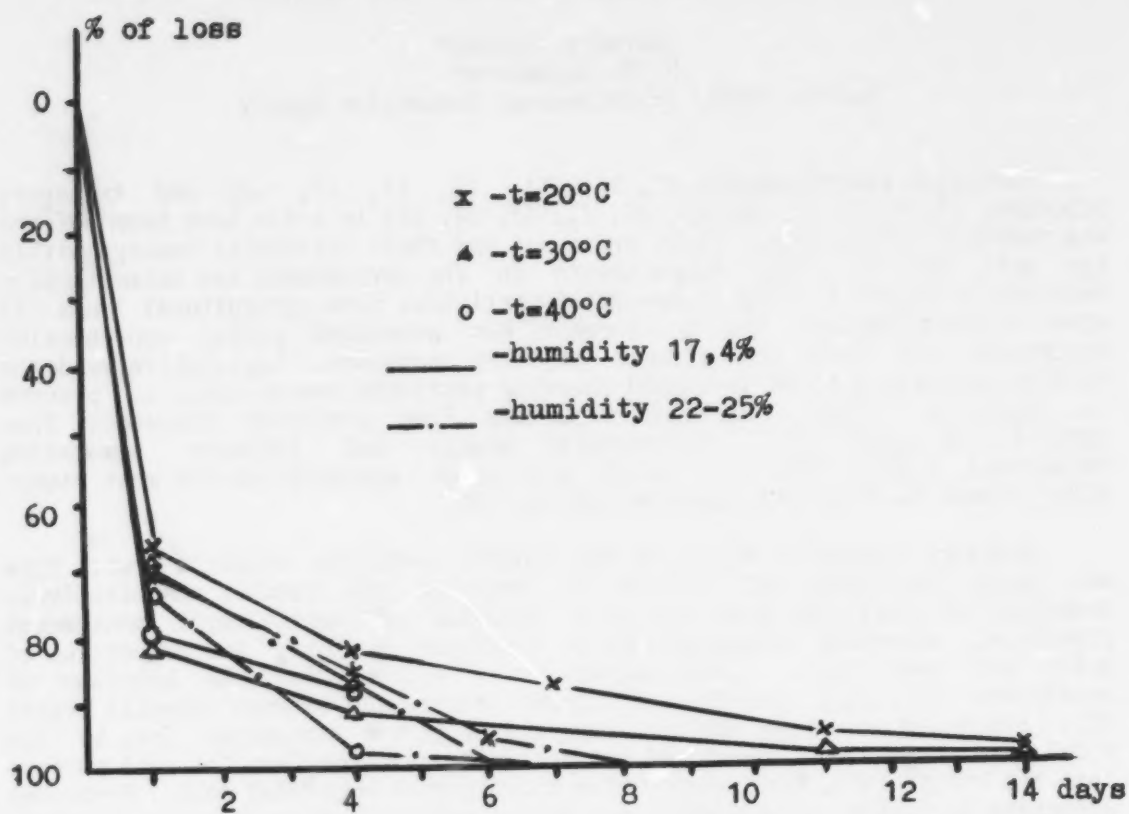


Figure 4. The dependence of the altosid persistence in the soil on temperature and humidity.



PREDICTING AND SIMULATING PESTICIDE TRANSPORT FROM AGRICULTURAL LAND:  
MATHEMATICAL MODEL DEVELOPMENT AND TESTING

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Pesticide transformation (7, 11, 14, 15, 16, 17, 19) and transport processes (3, 4, 9, 12, 13, 18, 20, 21, 22, 24, 25) in soils have been defined and reviewed extensively. These processes and their interrelationships within the soil and to other compartments in the environment are schematically depicted in Figure 1. The transport of pesticides from agricultural lands and other compartments of the environment has generated public apprehension concerning the fate and effects of these compounds. Legislative mandates require guidelines to be developed covering pesticide use in order to prevent or minimize water pollution resulting from pesticide transport from agricultural land (26). Mathematical models and computer simulation techniques rather than the trial and error approach are the most viable alternatives to arrive at these guidelines (2).

Computer simulation models of the dynamic multiple rainfall-event type are being developed and refined to describe and predict quantitatively transport of pesticides from soil as a function of agricultural management practices, watershed characteristics, climatic factors, and properties of soils and pesticides. These models must account for the behavior of pesticides in soils during each rainfall event, and between rainfall events (2). Processes occurring during a rainfall event and accounted for by the model are downward movement and net pesticide transfer from the soil surface into the runoff film, both in solution and adsorbed on eroded soil. Processes affecting pesticide concentration and phase redistribution between rainfall events include evaporation, adsorption, desorption, net pesticide movement under conditions of unsaturated flow, and chemical, microbial, and photochemical transformation processes, volatilization, and organism uptake.

Models capable of predicting at two areal scales are required: (a) at the farm-unit size watershed scale (hectares) to assess the effectiveness of agricultural practices and alternative control measures to control water pollution and (b) at a basin-scale (square kilometers) to predict the contribution of multiple agricultural land use on water quality.

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Steps involved in model development, testing and verification will be discussed in detail and include (a) system definition (Figure 2) and formulation of a conceptual model (2); (b) assemblage of a multidisciplinary, multi-institutional research team and the integration of team efforts; (c) selection, design and instrumentation of 1-3 ha farm-unit size watersheds and 36-48 km<sup>2</sup> size watersheds; (d) design and installation of highly instrumented, small experimental plots (6 X 9 m) to study pesticide degradation kinetics as a function of soil properties and meteorological parameters (23); (e) development of data handling and computerized data processing programs; (f) selection of experimental pesticides to "track" four major modes of transport; (g) development of rapid, sensitive, integrated analytical methods; (h) selection of agricultural management practices and compatible cropping systems; (i) continuous monitoring of meteorological parameters, soil, water and pesticide loss during runoff events and the determination of pesticide spatial and temporal distribution vertically and horizontally over the watersheds for a period of three to four years; (j) development of algorithms for adsorption/desorption, pesticide degradation, volatilization, snow accumulation and snowmelt and pesticide mass transfer coefficients from soil to runoff waters; (k) interfacing these algorithms to the basic hydrologic and soil loss routines; (l) programming, calibration, and testing of the overall model; (m) sensitivity analysis of selected model parameters; (n) specific parameter generation, e.g., adsorption/desorption isotherms for a variety of pesticides and edaphic conditions; and (o) verification of the overall model at both areal scales in different geographic regions using either "new" or split data sets.

Four basic pesticide runoff models have been developed and tested to varying degrees (1, 5, 6, 10) and one refined and updated to include snow accumulation, snowmelt runoff, and nutrient transformation and transport (8).

The structure and operation (Figure 3) flow chart (Figure 4), input/output requirements, sample results, simulative capability and observed problems or deficiencies for a farm-unit size watershed scale pesticide transport model (8) using the lumped parameters/statistical approach will be discussed.

Approaches and problems for model scale-up and interfacing to basin-scale water quality model will be treated.

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# TRANSPORT AND FATE OF PESTICIDES IN THE ENVIRONMENT

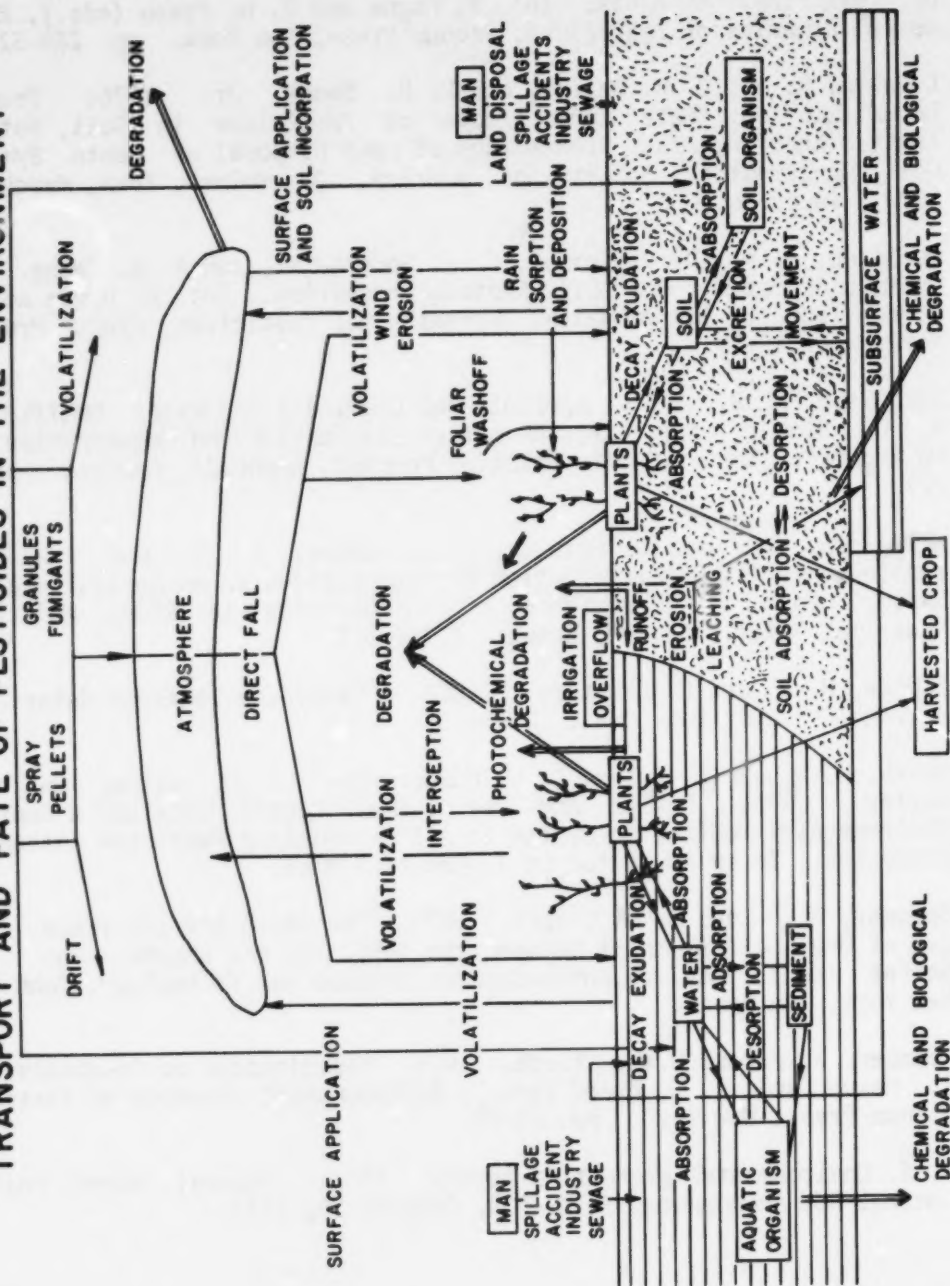


Figure 1. Transport and fate of pesticides in the environment (18).



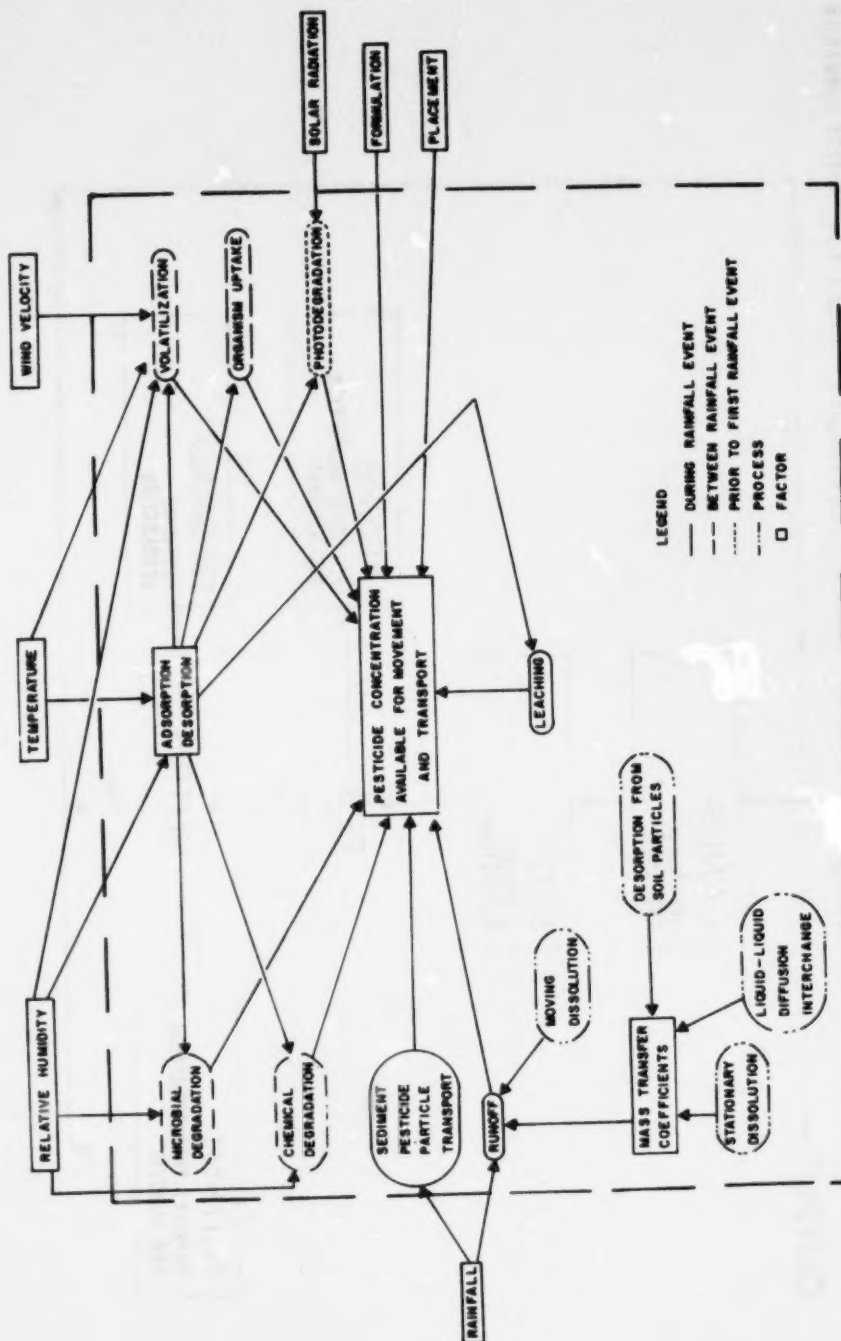


Figure 2. Processes and factors which determine the concentration of pesticide available for runoff from agricultural land. Climatic factors lying outside of the dashed lines are exogenous with respect to the soil-pesticide system (2).

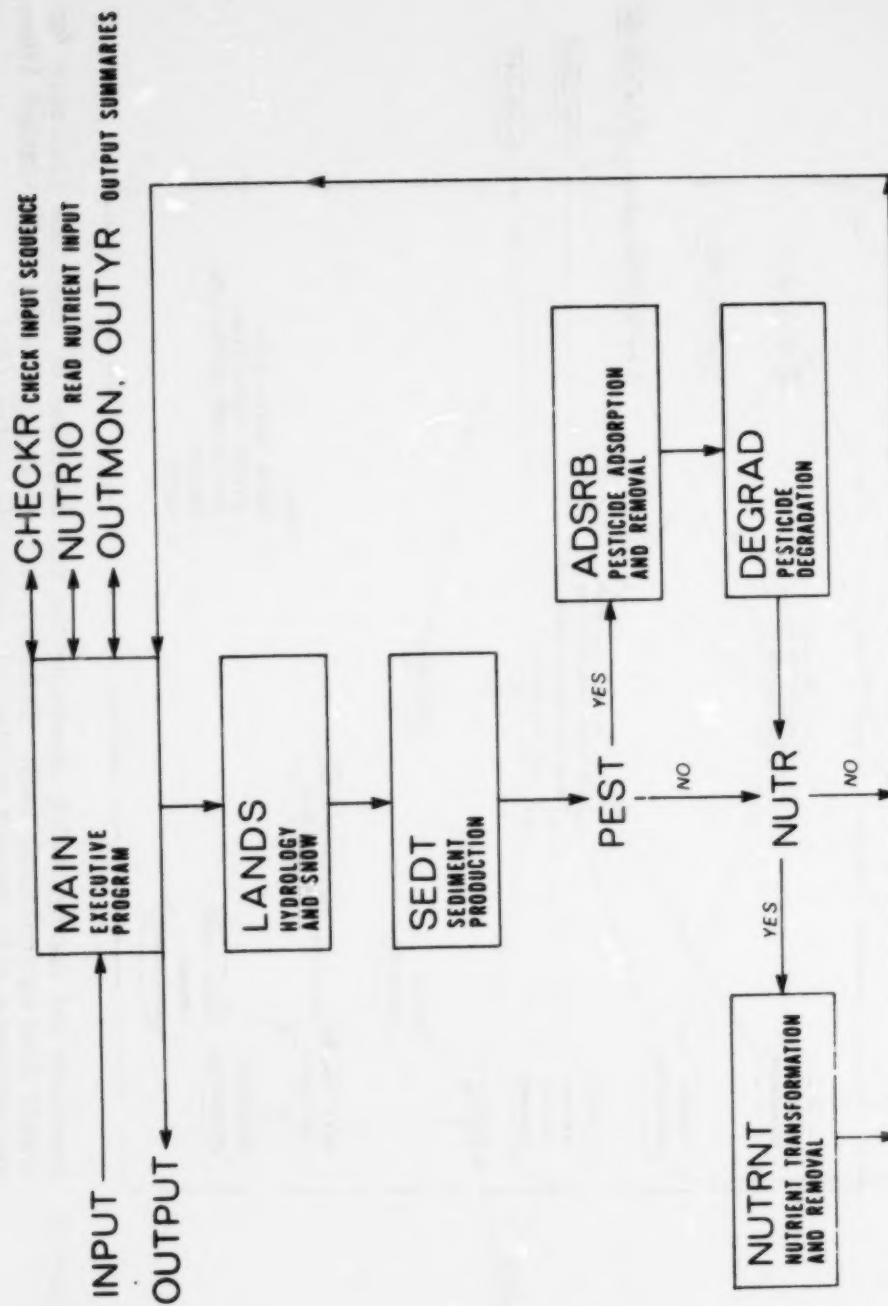


Figure 3. ARM model structure and operation (8).



**GENERAL LAWS OF THE MIGRATION OF PESTICIDE  
RESIDUES IN THE DELTA LANDSCAPE UNDER  
IRRIGATION**

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Migration and transport of both, the atoms of the elements and the natural compounds are, in the opinion of V.I.Vernadski (1927), one of the geochemical laws of biosphere. This universally observed process has lately been involving various xenobiotics introduced artificially into the landscape, e.g. pesticides, the products of their transformation and destruction. V.A.Kovda (1975) suggests that the process of migration determines diverse aftereffects caused by biocides and other xenobiotics (landscape-regional, regional-basin and global ones) in the biosphere.

Migration can be characterized as a complex of processes of redistribution of xenobiotics (and the products of their transformation) in space and in time (A.E.Persman, 1933; V.L.Anokhin, 1974). In the process of redistribution a pesticide can be transformed into various products. The leftovers of the parent compound together with the products of its transformation are defined as pesticide residues.

Xenobiotics are mainly transported in aquatic medium, in atmosphere and through organism migration. In the aquatic medium xenobiotics are transported with the surface and subsurface runoff. In the first case, the compounds are transported in the form of a liquid runoff (true solutions of electrolytes, compounds with neutral molecules, and colloidal solutions), and in the form



of a solid runoff (suspensions, sorbed substances with precolloidal particles or organo-mineral colloids). The subsurface transport of xenobiotics is carried out principally in the form of a liquid runoff (V.A.Kovda, 1974; M.A.Glazovskaya, 1972). Under the conditions of the delta irrigated landscapes the water runoff is controlled, the surface runoff to a greater, and the subsurface runoff to a lesser degree. The transport of large water masses by these pathways is, consequently, of a clearly defined seasonal character.

Transport of toxicants by the subsurface runoff is usually underestimated on the account that the rates of ground water flows are incomparable to the water velocity in rivers or canals of the open irrigation system. That is really so, and under the conditions of the time-limited parameters the intrasoil transport may be neglected, especially, in case of a point pollution source. Under the conditions of large rice irrigation systems the coefficients of land-use reach maximum values (over 50%) as well as the crop rotation saturation with rice (60-70%). And the rice is being treated with the same preparations for many years. That is why the subsurface transport of pesticide residues here should always be taken into consideration. Evidently, the larger is the territory treated with pesticides, the greater its evaporation and filtration losses, the heavier would be the share of pesticide residues transported with the subsurface runoff. Thus, in the USSR as a whole the subsurface runoff calculated per water constituent amounts to only 25%, while the share of the total ion subsurface runoff is over 50%. Even more dramatic figures have been found for the internal drainage basin of the Aral sea which has 83% migrants per subsurface ion runoff ("Migration of Chemical Elements in the Ground Water of the USSR. Laws and Quantitative Estimation", Moscow, 1974).

The runoff driving force is determined with the help of the gradient of water level in a water source (a river, an irrigation canal, a water reservoir) and in a water-receiving reservoir (a sea, a lake, a river, a trunk canal). While approaching the water-receiving reservoir the absolute values of water levels in the open sys-



tem diminish reaching zero and negative values at some areas. Operation of the hydrotechnical constructions (pump house stations), however, maintains the surface runoff at the required level. The transport of substances by the subsurface runoff is consequently slowed down. A similar picture is characteristic of the period of intensive use of irrigation systems (the growing season). After harvest only a small part of the surface runoff (unlike the subsurface runoff) is retained in some elements of the natural hydrographic system. The action of the surface and subsurface runoff results in the creation of a zone of secondary accumulation (redeposition) of pesticide residues in the natural conditions (V.A.Kovda, 1975; B.P.Strekozov et al., 1977; M.S.Sokolov, 1977).

The mechanisms of toxicant transport with surface and subsurface runoff are greatly influenced by nature and by peculiarities of ground composition. V.L.Anokhin (1974) distinguishes the following four cases: free transport of the migrant without delay in the filter layer; mechanical filtration of the suspended coarse-dispersed particles of the migrant-carrier (colmatage); coagulation and sedimentation of the colloidal-dispersed particles on the contact border of the liquid and solid phases; dissolving of the component on the solid phase surface (leaching) or its reverse process, chemisorption. V.B.Zaitsev (1975) distinguishes several principal types of ground water occurrence to be considered in rice irrigation with flooding, and two basically different regimes of ground water under the flooded rice field: with joining irrigation (surface) and ground waters and a non-joining regime during the whole growing season.

Many scientists investigate the peculiarities of vertical migration of pesticides and other xenobiotics in the ground with undisturbed structure using the techniques borrowed from the soil science, e.g. the method of the so-called "flooded sites", or "flooded sashes". We also employed this method and got some information on the peculiarities of movement of the main herbicides applied in rice breeding and certain products of their transformation, over the water-saturated profile of the meadow-chnozem-

like soil (M.S.Sokolov et al., 1974). On the basis of these data and experiments on sorption under the static conditions we arrived at the conclusion that any chance of the herbicide residues entering the ground water is practically excluded. However, the experiments on water analyzing in sash drainage canals (M.S.Sokolov et al 1974) and the experiments with observation wells drilled in the rice field and nearby, at different depths (from 0.5 to 2.5 m) as well as the use of special appliances for sampling interstitial solutions of the upper undisturbed layer of the ground (at 0.2-0.5 m depth) proved the contrary (Nevzorov et al., 1975; M.S.Sokolov et al., 1977). Comparatively small quantities (up to 1% of the introduced dose, in average) of the residues of propanil and molinate migrate with the irrigation water along the pores, cracks or cavities into the lower-lying soil horizons. This fact emphasizes the necessity of taking into account both, the microstructure and the macrocomposition of the soil and subsoil while characterizing the soil profile. Transport of water and water-contained substances downward (along the soil profile) is achieved due to the gravity (percolation, filtration) and diffusion forces. However, the contribution of the latter into the migration process is negligible.

The rate of the vertical percolation is determined by the value of the porous spacing in the ground, peculiarities of its structure, as well as by the level and type of ground water occurrence (V.B.Zaitsev, 1975; I.G.Aliev, 1976). In general, the distribution of the migrant along the soil profile and over various ground-water horizons is described with the help of the exponential law. The distribution zone of the migrant usually lags behind the water movement even under the leaching irrigation regime due to the non-saturation of the soil absorbing complex in the thickness of porous spacing.

The irrigation system and various types of drainage intensify the intrasoil (spatial and vertical) transport of pesticide residues thanks to the lowering of the ground water level. Observation wells drilled perpendicular to the trunk canal helped to examine the dynamics of the herbicide residues content in the ground water.

It appeared that in the close vicinity of a canal (a drain) the substance concentrations in the ground flow and in the canal water are close (M.S.Sokolov et al., 1975; A.P.Chubenko, B.P.Strekozov, 1976; A.P.Chubenko, 1975; 1976). That can be observed in cases when the flows of ground water and canal water are comparable. In case of the ground water flow polluted with herbicide residues, moving along the natural slope of the locality towards water intakes, the content of toxicants in the subsurface runoff is not directly connected with their concentration in the open collector system. The fact is explained not only by the difference in the water flows but also by the different buffer action and self-purification capacity of the landscape. The buffer action of these two processes is stipulated by abiotic and biotic factors (A.N.Tjurjukanov, 1964; A.I.Perelman, 1973). Their action is very often manifested in the natural and irrigation water, in soil and subsoil, in the bottom deposits and biota, simultaneously and in correlation. Among the abiotic factors the main part in the buffer action is played by sorption, among the biotic factors, by metabolic processes. The buffer action regulated by the abiotic factors sharply decreases with the reduction of water exchange, in the absence of insolation and during salinization. With the lowering into the soil and subsoil the role of the biotic factors in the buffer action decreases too. Evidently, the conditions of self-purification of the ground water unlike those of the surface water are extremely unfavourable on the account of constant temperature, increased salinity, impoverished microflora, absence of substrates for co-oxidation, extreme values of pH, absence of conditions necessary for photochemical transformations and, lastly, more pronounced anaerobic conditions. All this promotes a prolonged retention of toxicants in the ground flow. Unfortunately, these specific conditions are never considered while staging modelling experiments on the subsoil.

The transport of pesticide residues with the surface solid runoff and the fate of the migrant "buried" with the benthal sludge



and subcolloidal particles of the shelf and estuarine zones of water intakes of the returned irrigation water are not sufficiently studied either. It turned out that propanil and 3,4-DCA (the principal product of herbicide transformation) are effectively sorbed by the sludge and clay fractions of the meadow-chnozer-like soil (M.S.Sokolov et al., 1974). The toxicants in the sorbed state are transported over large distances along the units of the irrigated system where the greater part of the accumulation and redeposition of the suspended matter occurs (B.P.Strekozov et al., 1975). However, the heaviest fraction settles down in the so-called clarification area of the water intakes, in the absence of water current. As the absolute content of propanil residues in the benthic deposits turns to be small (0-0.7 mg/kg), their concentration in the firth water is much lower than the maximum permissible one (B.P.Strekozov et al., 1977; M.S.Sokolov et al., 1977). But due to the unfavourable conditions of decomposition and desorption there should go on a slow but constant process of toxicant cumulation. Therefore, under the circumstances, it is necessary to anticipate the immediate and remote aftereffects of this cumulation.

To make clear the mechanism or at least the essential feature of the self-purification process of the landscape and its separate elements, balance experiments are required. As a result of such experiments on propanil (M.S.Sokolov et al., 1976) and MCPA (Dr. D.Crosby, 1975) important and interesting information was obtained that permits to trace the fate of a herbicide in the landscape and to even replan the strategy of its application. Evidently, only the full-scale experiments can provide us with the reliable data on pesticide residue transport with the surface and subsurface runoff, as well as with the data on self-purification of the landscape and its elements. These are labour-consuming and costly experiments that require careful preparation. Simultaneously we should not neglect important supplementary information that is to be obtained through experimental ecotoxicological modelling (M.S.Sokolov, 1975). Practically, only these methods will make us

capable of solving the tasks of a multifactor experiment.

As, on the whole, the anthropogenic process of the transport of pesticide residues in the landscape and the natural process of self-purification are of an oppositely directed and seasonally expressed character, it is extremely important to correctly forecast the conditions limiting these processes. The role of the natural complex process of self-purification can never be overestimated. Therefore, it is necessary not only to study and develop the methods of calculating the levels of maximum toxicant load-capacity of the landscape (Yu.A.Izraelle, 1974) and the most favourable conditions for self-purification (G.K.Gryzlova, 1975), but also to store the data on the laws of transport of various pollutants.

A well-known Soviet geochemist and geologist, academician A.E.Fersman wrote that the phenomenon of transport of elements appears to be the most important object for geochemical research, as it determines the whole association of the nature phenomena, their diversity and peculiarities. In the same way, the research in the field of ecotoxicology of pesticides and other xenobiotics, examination of their fate, transformation, forms, pathways and mechanisms of transport seem to us extremely important and necessary from the point of view of rational utilization of the natural resources of biosphere and its conservation.

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CERTAIN LAWS OF ORGANOCHLORINE PESTICIDE REDISTRIBUTION  
IN THE SOIL-WATER, SOIL-PLANT SYSTEM

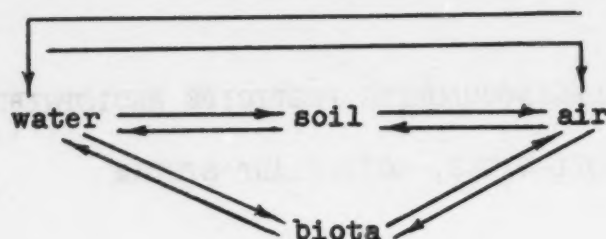
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It has been known that organochlorine pesticides are used by man for about 25-35 years, first - as a means for combatting insects-carriers of diseases of people and domestic animals and then - for plant protection on a large scale. Rather recently, as highly sensitive methods of analysis are mastered, the scientists have concentrated their attention on the fact that pesticide residual amounts are globally being found everywhere - in plants, soil, water, birds, fish, and air. During the years that followed a danger of further environmental contamination with stable pesticides caused certain limitation (and for DDT - a ban) of their use and led to the widescale scientific search for understanding the process of transfer of these pesticides in the environment, their fate in various phases of the environment, and their hazard for man and biota as a whole.

Organochlorine pesticides belong to those chemicals which are the most persistent in the environment. This property primarily ac-

counts for the fact of their global finding in all phases of the environment. Studies of the pesticide dynamics in the cycle



and acquisition of the quantitative characteristics of their redistribution in various phases are of evident interest, first - from the viewpoint of predicting variations of the levels of pesticide residual amounts in the media mentioned, and second - because in the long run it will provide more information on pesticide persistence in the environment as a whole. In the cycle being considered soil is the major component of the biosphere determining the adjacent medium contamination.

This paper presents the experimental data on pesticide evaporation from water and soil, and their transport into plants. Investigations were carried out with the pesticides which had been most widely used in the previous years, their physical and chemical properties being well studied, such as DDT and BHC. In the last few years the process of pesticide evaporation from soils and various surfaces has received considerable attention. It has been found that evaporation and vapor-phase transport are important elements of dissipation even of the so called non-volatile pesticides, such as DDT, dieldrin, and others. We set a problem - to find the simplest method



of estimating pesticide evaporation from soils, water, and surfaces. Earlier it has been found that the rate of pesticide evaporation from the moist soils and moistened surfaces is considerably higher than that without moistening [1-4]. Acree and co-workers [5,6] found that DDT is capable of co-evaporating in considerable amounts with the water from water solutions. These and other works indicate that apparently, the rate of pesticide evaporation can be determined quantitatively from the rates of water evaporation from the surfaces of soil, water, and other objects.

In the first stage of work we have obtained a quantitative assessment of the DDT and BHC evaporation from the water solutions. The DDT and BHC concentrations in water were investigated over the range 1 to 130 mg/l for DDT and 0.1 to 1000 mg/l for BHC. The experiments were carried out in the thermostatic vacuum installation. The products of evaporation were freeze-dried in the trap being cooled by liquid nitrogen. The pesticides were extracted by n-hexane and analyzed by the method of gas-liquid chromatography. Over the range of low DDT concentrations the experiments were conducted with the  $^{14}\text{C}$ -labeled pesticides. The results obtained are presented in Figures 1 and 2. It is evident that the curves of relationships between the evaporated pesticides per gram of water and their concentrations in water have two distinctive portions: one adhered to linear dependence on pesticide concentration in water and the other independent of it, that is the portion of saturation. The amounts of co-evaporated pesticides per gram of water on the portion of saturation at 20°C are 0.31, 12.6, and 42  $\mu\text{g}$  for p,p'-DDT,  $\gamma$ -BHC, and  $\alpha$ -BHC,

respectively. For this portion, our experimental data are rather adequately correlated with the values calculated theoretically with the known relationship which is used in steam distillation of two mutually insoluble liquids:

$$\frac{W_A}{W_B} = \frac{M_A P_A}{M_B P_B}$$

where W, M, and P are the weight, molecular weight, and pressure of pesticide and water saturated vapor, respectively.

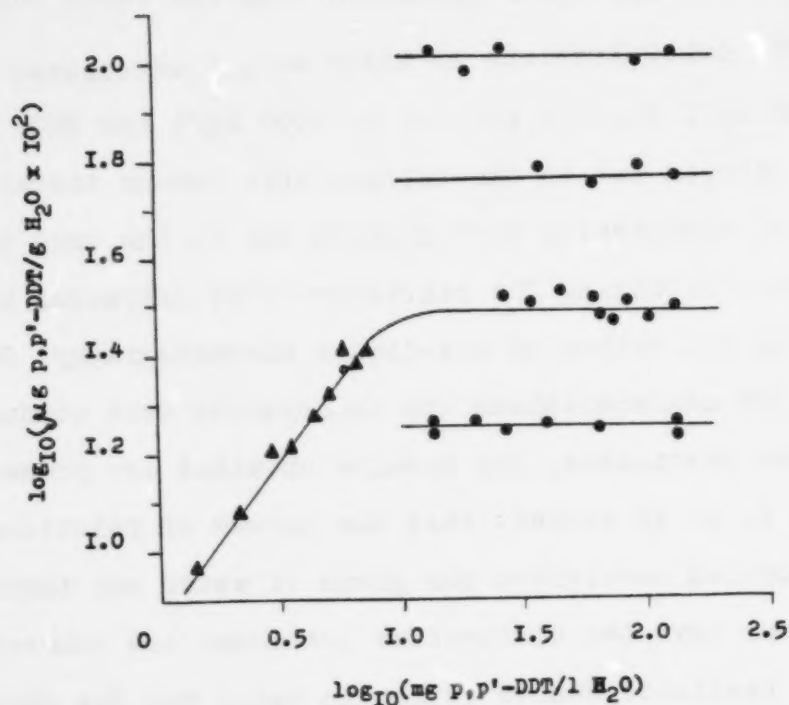


Figure I. Co-evaporation of p,p'-DDT with water at various temperatures (triangles - radiometric method of analysis, circles - chromatographic method).

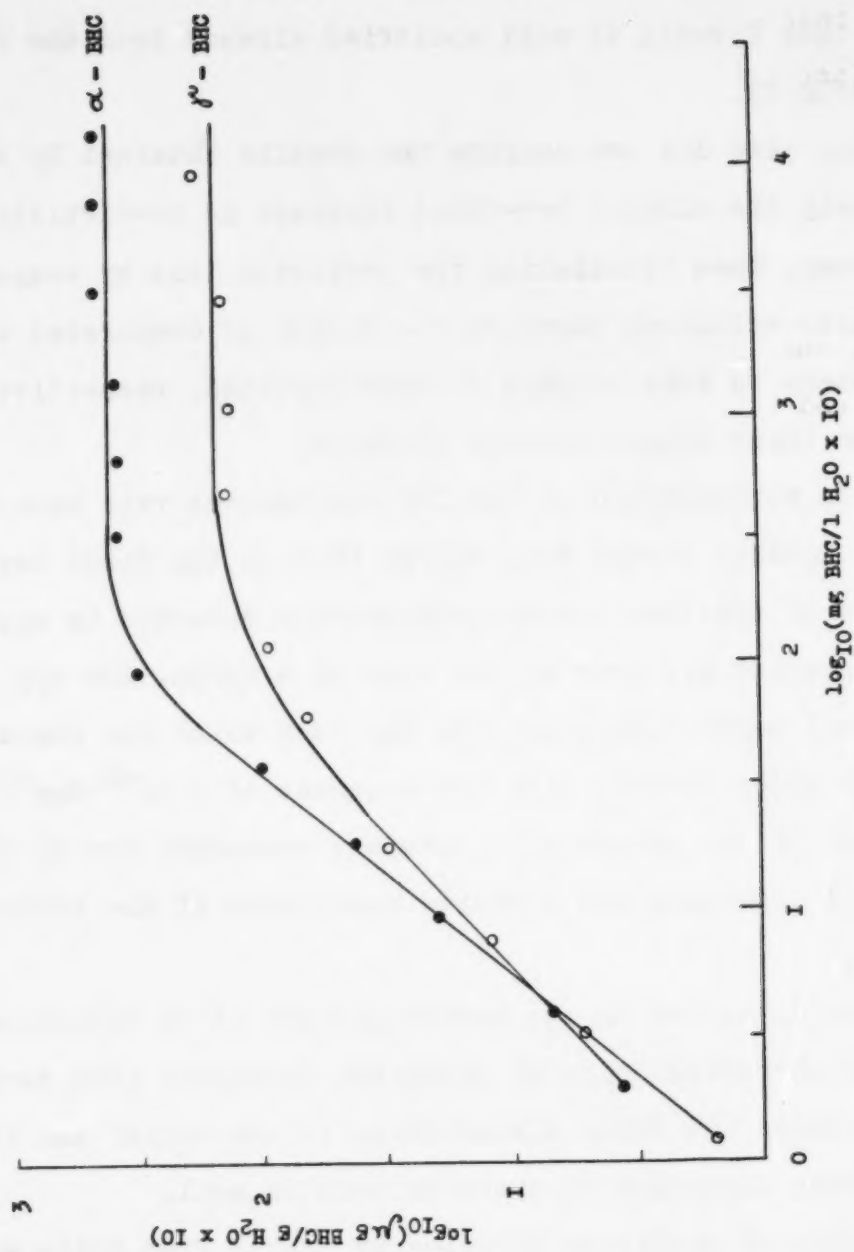


Figure 2. Co-evaporation of  $\gamma$ -BHC and  $\alpha$ -BHC with water at 20°C.

The temperature characteristic of the p,p'-DDT co-evaporation on the portion of saturation over the temperature interval 10 to 40°C shows that this formula is well satisfied already over the range 30 to 40°C (Table I).

Thus, our data did not confirm the results obtained by Acree and Bowman, namely the alleged 3-8-times increase in co-distillation of DDT with water. When calculating the pesticide loss by evaporation from the water solutions based on the amount of evaporated water, it is necessary to take account of both portions, respectively, proceeding from their concentrations in water.

The field measurements of the DDT evaporation rate under its surface application in the soil showed that on the first day the average rate of DDT loss through evaporation amounted to approximately one percent per hour at the rate of 2 kg/ha. DDT applied in the 10 cm soil layer disappeared at the rate which was characterized by the first order process with the constant of  $5 \cdot 10^{-2} \text{ day}^{-1}$ . So large a value of the constant is possibly accounted for by the substantial soil loosening and climatic conditions of the process being studied.

The other direction of our investigations is to determine the quantitative characteristics of pesticide transport into various species of plants and their distribution in the aerial and root parts of plants depending on their content in soil.

The problem of pesticide sorption by plants from soils was discussed in several publications [7-9], this problem being considered from the viewpoint of both hygienic rationing of pesticide appli-



Table I. Theoretical and experimental values of the co-evaporation of p,p'-DDT, p'-BHC, and  $\alpha$ -BHC with water

| Pesticide     | Temperature,<br>°C | Pesticide<br>vapor<br>pressure,<br>mm Hg | Water<br>vapor<br>pressure,<br>mm Hg | Co-evaporation, mg/g H <sub>2</sub> O          |              |
|---------------|--------------------|------------------------------------------|--------------------------------------|------------------------------------------------|--------------|
|               |                    |                                          |                                      | theoretical<br>(calculated<br>with equation I) | experimental |
| p,p'-DDT      | 10                 | $2.61 \times 10^{-8}$                    | 9.2                                  | 0.056                                          | 0.17         |
| p,p'-DDT      | 20                 | $1.48 \times 10^{-7}$                    | 17.4                                 | 0.16                                           | 0.31         |
| p,p'-DDT      | 30                 | $7.18 \times 10^{-7}$                    | 31.6                                 | 0.44                                           | 0.58         |
| p,p'-DDT      | 40                 | $3.23 \times 10^{-6}$                    | 54.9                                 | 1.15                                           | 1.02         |
| p'-BHC        | 20                 | $9.4 \times 10^{-6}$                     | 17.4                                 | 8.76                                           | 12.8         |
| $\alpha$ -BHC | 20                 | -                                        | 17.4                                 | -                                              | 42           |

cation and their metabolism, accumulation in plants, etc. However, there are rather few quantitative assessments characterizing the degree of pesticide sorption by plants depending on the levels of their concentration in soil. The work by Voerman and Bessemer [9] appeared to be one of the most significant in this field. The authors provided a quantitative information on the degree of sorption of several pesticides (dieldrin, lindane, DDT) from the soil by plants (grass) and their distribution in the aerial and root parts of plants.

Our experimental data are concerned with the sorption of DDT and related compounds by such plants as barley and clover. The concentrations of DDT and related compounds were investigated over the range 2 to 8 mg/kg of soil, technical DDT containing 74.3% p,p'-DDT, 22%  $\sum$  o,p'-DDT, p,p'-DDD, and 3.7% p,p'-DDE. The experiments were carried out in the vegetative pots with three repetitions. In a month for barley and in two months and a half for clover the samples of soil and plants were collected, the vegetation being analyzed in parts: roots and green mass.

The results of investigations are given in Tables 2,3 and in Figures 3,4. They indicate that the degree of the DDT and related compounds entering the plants depends on the rate of pesticide application into the soil. The pesticide accumulation in the green mass of plants slightly varies over the range of rates being studied - within the limits of 6-15% (in relative units of the  $\sum$  DDT per kg of green mass to the  $\sum$  DDT per kg of soil). A picture of the root system sorption is completely different. The ratio of concent-

Table 2. Dependence of the DDT products accumulation (mg/kg of dry weight) in roots and stems of barley on the rates of pesticide application in the soil. Duration of the experiment is 1 month.

| Rate of application, mg/kg of soil | Object of investigation | P,p'-DDT | o,p'-DDT plus P,p'-DDD | p,p'-DDE | $\frac{\sum \text{DDT (roots)}}{\text{rate of application}}$ |                           |
|------------------------------------|-------------------------|----------|------------------------|----------|--------------------------------------------------------------|---------------------------|
|                                    |                         |          |                        |          | $\sum \text{DDT (roots)}$                                    | $\sum \text{DDT (stems)}$ |
| 2                                  | Soil                    | 1.00     | 0.35                   | 0.04     | 5.03                                                         | 33.6                      |
|                                    | Roots                   | 7.21     | 2.68                   | 0.18     |                                                              |                           |
|                                    | Stems                   | 0.24     | 0.04                   | 0.02     |                                                              |                           |
| 4                                  | Soil                    | 2.04     | 0.67                   | 0.06     | 7.22                                                         | 100.7                     |
|                                    | Roots                   | 19.71    | 8.40                   | 0.78     |                                                              |                           |
|                                    | Stems                   | 0.20     | 0.05                   | 0.02     |                                                              |                           |
| 6                                  | Soil                    | 3.16     | 1.13                   | 0.09     | 8.55                                                         | 160.0                     |
|                                    | Roots                   | 34.4     | 15.3                   | 1.53     |                                                              |                           |
|                                    | Stems                   | 0.11     | 0.08                   | 0.03     |                                                              |                           |
| 8                                  | Soil                    | 4.32     | 1.53                   | 0.17     | 10.55                                                        | 169.0                     |
|                                    | Roots                   | 57.5     | 24.2                   | 2.50     |                                                              |                           |
|                                    | Stems                   | 0.35     | 0.12                   | 0.03     |                                                              |                           |

Table 3. Dependence of the DDT products accumulation (mg/kg of dry weight) in roots and stems of clover on the rates of pesticide application in the soil. Duration of the experiment is 2.5 months.

| Rate of DDT application, mg/kg of soil | Object of investigation | p,p'-DDT | o,p'-DDT plus p,p'-DDD | p,p'-DDE | DDT (roots)         |             |
|----------------------------------------|-------------------------|----------|------------------------|----------|---------------------|-------------|
|                                        |                         |          |                        |          | rate of application | DDT (stems) |
| 2                                      | Soil                    | 1.18     | 0.37                   | 0.037    | 4.5                 | 37.5        |
|                                        | Roots                   | 6.1      | 2.6                    | 0.32     |                     |             |
|                                        | Stems                   | 0.18     | 0.04                   | 0.02     |                     |             |
| 4                                      | Soil                    | 1.67     | 0.61                   | 0.08     | 5.9                 | 138.0       |
|                                        | Roots                   | 15.0     | 7.6                    | 1.0      |                     |             |
|                                        | Stems                   | 0.13     | 0.03                   | 0.012    |                     |             |
| 6                                      | Soil                    | 3.11     | 0.79                   | 0.16     | 7.4                 | 201.8       |
|                                        | Roots                   | 29.3     | 12.7                   | 2.4      |                     |             |
|                                        | Stems                   | 0.15     | 0.06                   | 0.013    |                     |             |
| 8                                      | Soil                    | 4.4      | 1.8                    | 0.21     | 8.3                 | 265.8       |
|                                        | Roots                   | 44.0     | 19.3                   | 3.1      |                     |             |
|                                        | Stems                   | 0.17     | 0.06                   | 0.02     |                     |             |



ratios of the sum of DDT products in roots to those in soil which is conventionally called the transport coefficient increases in a greater degree as the content of these products in soil increases. The data obtained by the authors mentioned above are shown in Figure 3 as triangles (the calculation has been performed by us). It is seen from the tables that the ratio of the DDT concentrations in roots to those in stems noticeably increases with the rates of pesticide application into soil and ranges from 33.6 to 169.0 units for barley and from 37.5 to 266.0 units for clover.

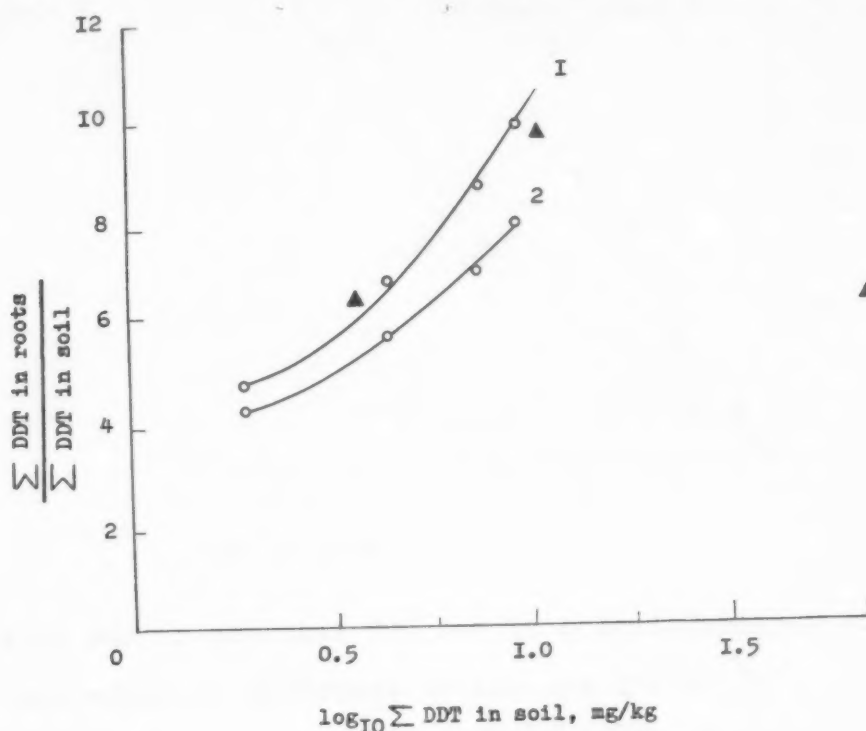


Figure 3. Dependence of the coefficient of DDT and related compounds transport (accumulation) in the roots of barley and clover on their content in the soil (1 - for barley, 2 - for clover).

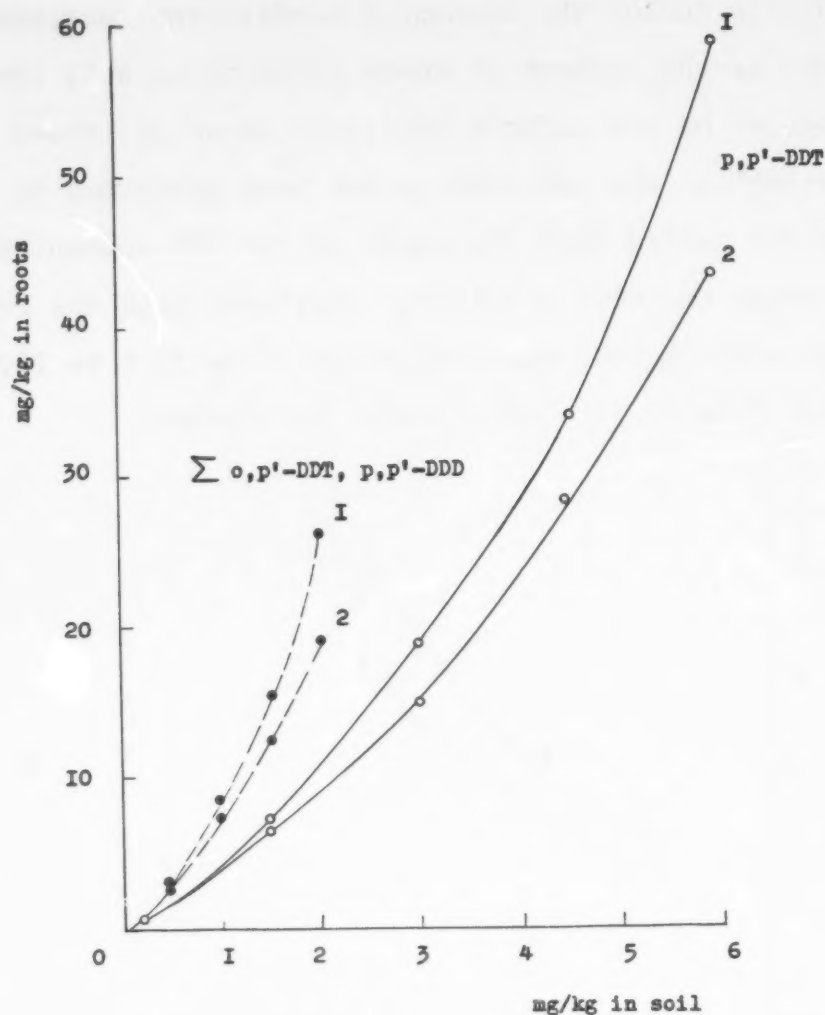


Figure 4. Accumulation of the DDT products in the roots of barley and clover depending on their concentrations in the soil:

1 - for barley (duration of the experiment is 1 month);

2 - for clover (duration of the experiment is 2.5 months).

Figure 4 indicates that accumulation of p,p'-DDT and the sum of o,p'-DDT and p,p'-DDD occurs at different rates as their concentrations in soil vary.

Analysis of the soil for the content of DDT products in it before and after an experiment indicates that over the time of the experiment their percentage composition did not practically changed. However, over the time of the experiments the loss of pesticides from the soils amounted to approximately 25%. It is possible that these losses are due to the process of evaporation.

Comparison of the results of our investigations with the data obtained by Voerman and others for different soils and species of plants as well as under different experimental conditions shows that either the mechanism of the DDT products entering the roots of plants from the soil is likely to be independent of the experimental conditions, types of soils, and species of plants or these conditions were similar. Further investigations at various types of soils and species of plants will provide opportunities to draw an appropriate conclusion about that.

Thus, using barley and clover as the objects of investigations we found that DDT and related compounds are mainly accumulated in the root system of plants.

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## PESTICIDE TRANSPORT AND METABOLISM IN MODEL SYSTEMS

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Laboratory studies devoted to investigating the environmental fate of pesticides have usually examined individual processes such as microbial metabolism, soil leaching, surface and vapor phase photodecomposition, volatilization from plant or soil surfaces, and plant uptake. In the environment, however, all of these processes may be operative on the molecule, so that in each stage of the pesticide dissipation process, one or more processes may play a major role. It has been extremely difficult to study two or more of these processes under controlled conditions which will enable a clear understanding of the contribution of each. Simplified model laboratory systems are now being developed which enable simultaneous measurement of numerous factors affecting pesticide dissipation in the environment.

### BIOLOGICAL AND CHEMICAL ASSAYS

Biological and chemical assays have been primarily used to study persistence, adsorption, and movement of pesticides through soil, and the effects of various soil and environmental conditions and properties on pesticide behavior in soil. Chemical assays are useful in both quantitative and qualitative determinations of pesticide residues, but are generally limited by the ability of the solvents to extract the residues from soil. Chemical analyses for pesticides and their degradation products in the environment was for a long time one of the major stumbling blocks in pesticide research. With the development of new instrumentation and procedures it is now possible to determine quantities of pesticides as low as a few parts per billion. Spectrophotometric and chromatographic instruments have become the major analytical tools in determining pesticides and their degradation products.

Bioassays are generally used as a quantitative measurement of the biologically active concentration of a pesticide known to be present. Bioassays involve the measurement of a biological response by living plant, microbe, or animal organisms in order to determine the presence and/or concentration of chemical in a substrate. For example, a soil bioassay involves the growing of an indicator organism in a pesticide treated soil, and then comparing the response of the test organism to similar organisms cultured in untreated soil or in soil containing known pesticide concentrations. Two basic assumptions are made when using bioassays: (a) that the organisms show increased injury in an order related to the pesticide concentration; and (b) that the responses obtained are reproducible.

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Bioassays and chemical-physical assays each contribute information of value and each are useful for certain circumstances. A major advantage of the bioassay is the assurance that the toxic activity of the pesticide molecule is what is being measured. It is not usually necessary to extract the pesticide from the substrate, thus circumventing the problems involved with the extraction procedures that are often needed for chemical assays. Bioassay procedures are usually more economical, less difficult to perform, and do not require as much expensive equipment as chemical and physical analytical methods. However, there are also difficulties in using organisms to bioassay for pesticides that must be considered when developing or using a bioassay. Growth is directly influenced by ambient environmental conditions such as light, temperature, watering method and level, and humidity. Variations in these factors may cause a greater biological response than the pesticide under test. Thus, the environmental and edaphic factors must be very closely controlled. Untreated organisms and known standards should be included each time an assay is conducted. Species variation in susceptibility to a given pesticide; and in some instances individual organism variation within a species may also be apparent. A comprehensive guide to bioassay, adsorption, absorption, leaching, and microbial interaction methodology has been published (1).

#### SOIL PERFUSION

Soil perfusion devices have been developed to study soil microbiological processes such as nitrification, denitrification, pesticide degradation, and microbial utilization of water-insoluble substrates such as sulfur or coal (2). The design shown in Figure 1 is equally adaptable to either positive or negative pressure systems. It has been used successfully with CO<sub>2</sub> traps both preceding and succeeding the system. Its principle advantages are: (a) adaptability to use with either positive or negative pressure systems; (b) ease of maintaining sterility if desired; (c) ease of sampling perfusate; (d) ease of controlling rate of perfusion; (e) adaptable to use with gases of known composition; (f) infrequent adjustment requirements; (g) self-supporting and compact design; and (h) relatively inexpensive parts.

This system has been used successfully to observe microbial degradation of pesticides (3,4). In such investigations, soils containing a pesticide were perfused with distilled water; or untreated soils were perfused with aqueous solutions of pesticides. Under these conditions degradation was determined either by measuring the rate of pesticide disappearance, or the accumulation of breakdown products, or by both. The kinetics involved with the degradation of a pesticide in similar systems have been discussed elsewhere (5,6). Typically, a lag period occurs during which there is no change in pesticide concentration, followed by a period of rapid disappearance of the pesticide (Figure 2). Subsequent additions of the pesticide decompose more rapidly than the first. This period of rapid breakdown is generally accompanied by proliferation of "effective" microorganisms capable of utilizing the pesticide as a sole or supplemental source of energy and carbon. Soils in which this phenomenon has occurred are frequently described as "enriched" soils (5). Isolation of pure cultures of effective organisms from enriched soils has been achieved via dilution plate techniques.

Data obtained with soil perfusion units have been primarily useful in assessing the relative biodegradability of pesticides (5,7); factors affecting microbial degradation of pesticides; microbial degradation of pesticide combinations (4); and soil enrichment and subsequent isolation of effective microorganisms. Other techniques are necessary for studying cometabolic or chemical processes involved with pesticide degradation in soil (8).

#### SOIL BIOMETRY

Several systems have been used to study degradation and metabolism of  $^{14}\text{C}$ -pesticides in soils. Two of these methods have been used extensively in our laboratory. Although either system can be used to study pesticide metabolism by isolated organisms, they are more commonly used with the total microbial population in soil considered as a tissue or unit organism. One system involves a "soil biometer" flask developed by Bartha and Pramer (Figure 3) (9). When  $^{14}\text{C}$ -labeled pesticides are incorporated into the soil, the apparatus and method of analysis enable both  $^{14}\text{CO}_2$  and total  $\text{CO}_2$  production to be monitored at frequent intervals for prolonged periods, and all measurements are made on the same soil sample without significant exposure to atmospheric  $\text{CO}_2$ . Although it was suggested by the developers that the magnitude of the difference in amount of  $\text{CO}_2$  produced by treated and untreated soil could be used as a measure of the extent to which an unlabeled pesticide molecule was oxidized, this approach may be inaccurate with pesticides which stimulate microbial activity in addition to serving as a substrate. Consequently, use of  $^{14}\text{C}$ -labeled pesticides provides a far more accurate indication of actual pesticide metabolism in soil.

The soil biometer flask has been used successfully to study microbial metabolism of numerous pesticides in soil. A serious limitation of this technique, however, may be encountered when volatile pesticides which can be trapped in base are examined in this system. It then becomes essential to determine by organic solvent extraction or precipitation of evolved  $\text{CO}_2$ , how much of the  $^{14}\text{C}$  material trapped in the base is actually  $^{14}\text{CO}_2$  or volatile  $^{14}\text{C}$ -pesticide residues. This problem is avoided in a system developed by Kearney and Kontson (10).

The system of Kearney and Kontson (10) permits simultaneous measurement of pesticide loss by volatilization and metabolic  $\text{CO}_2$  evolution from soils (Figure 4). The system is maintained with an air flow which flushes evolved  $\text{CO}_2$  and volatilized pesticide residues from the incubation flask. Each flask is equipped with a polyurethane foam plug held in a sintered glass filter funnel. This apparatus was used to examine vapor and metabolic loss of two dinitroaniline herbicides from soil (Table 1). A comparison of the KOH traps revealed no difference in the amount of  $^{14}\text{CO}_2$  trapped in the presence or absence of the polyurethane plugs. Analysis of the plugs divided into four sections showed that 97% of the butralin volatilized was recovered in the first centimeter of the plug and 1% of each of the remaining three 1-cm sections. Extraction of the KOH solutions with ethyl acetate revealed that no butralin escaped through the plug. Results obtained with this system indicated that loss of trifluralin by volatility from soil surfaces was the major loss mechanism during the first three weeks after application (Table 1) (10).



Before the system can be used with other pesticides, the trapping characteristics of the plugs should be tested. The system was easy to maintain although the soils lost moisture during the time between weekly samplings. This can be remedied, however, through the use of humidified air. It was suggested that studies on vapor phase photolysis might also be feasible in the system.

#### ROOT VS VAPOR SORPTION METHODOLOGY

Crops can be contaminated aerially by intentional, direct application of pesticides or by indirect ways such as spray or dust drift and wind-borne pesticide-treated soils. Some pesticides are root-absorbed directly from treated soil, then translocated to aerial portions of plants. Another possible pathway of contamination is pesticide vaporization from soil and sorption of these vapors by aerial portions of plants. Barrows et al. (11) found that the leaf-to stalk ratio of dieldrin concentrations in field-grown corn was about 50 times higher than the ratio found in insecticide vapor-protected plants grown in a greenhouse. They attributed this large difference to aerial contamination of the field grown corn.

Beall and Nash (12) developed a system for distinguishing between pesticide contamination of plants resulting from root sorption and plant sorption of the pesticide vapors emanating from the soil (Figure 5). Surface and sub-surface soil layers are separated by a water- and vapor-tight disk. To confine vapors around the plant, a polyethylene cage (open at the top) is provided. In any given pot only one pesticide is used, and only one of the soil layers is treated with pesticide. A hole (fitted with a piece of glass tubing) in the center of the disk allowed the plant stem to pass through the upper layer without touching the soil.

In experiments with several  $^{14}\text{C}$ -labeled insecticides they observed that regardless of the insecticide treatment, contamination of aerial plant parts occurred through both root and vapor sorption (Table 2). Although their research was performed under greenhouse conditions, the results indicated that insecticide volatilization from treated soil may be as important (dieldrin) or more important (DDT) than root uptake as a mechanism of crop contamination under field conditions. Actually, under field conditions, where roots are able to penetrate down into untreated soil, volatilization may be an even more important mechanism of contamination than their pot experiments demonstrated. Results from such a method contribute to a better understanding of the nature of root sorption and vapor sorption of pesticide residues by plants and their fate and behavior on or within the plant.

#### AGROECOSYSTEMS

Recently, agroecosystem chambers have been developed in which the combined effects of all pesticide dissipation processes can be studied (Figure 6) (13). Agroecosystems allow for independent study of dissipation processes in soil, plant, air, and water as a function of time. The agroecosystem shown here has a number of advantages, i.e. it is relatively inexpensive, easy to operate, monitor, and sample; versatile in the number of plants and soils that can be studied; adjustable to rainfall and potentially adjustable to



wind velocity, light intensity and duration; and conducive to balance studies where pesticide mobility can be compared under similar conditions. It has an advantage over previous systems because the large air exchange provides cooling, prevents moisture condensation on the chamber walls, and permits sufficient air sample volumes for measurement of very low residue concentration. The aerial residues in the exhaust air are trapped on polyurethane foam plugs, which are sampled periodically. Numerous other environmental factors such as temperature and relative humidity inside the chambers are monitored periodically with automatic equipment.

In initial investigations when toxaphene and DDT were applied to cotton in the agroecosystem chambers, 24 and 15%, respectively, were lost to the air; 20 and 24% were in the surface 1 cm of soil; and the rest remained on the cotton plants over a 90-day period. Calculated half-lives in air for toxaphene were 15.1 days, and 19.8 days for p,p'-DDT. More detailed accounts of these results have been published (14).

Initial objectives have been to test the ability of the agroecosystem for comparing the mobility of different classes of pesticides and thereby identifying potential environmental problems. Long-term objectives are to explore the possibilities of determining bioaccumulation of pesticides in terrestrial organisms and interfacing the agroecosystem with other model ecosystems, particularly the aquatic ecosystem. An ultimate objective is to devise methods of reducing pesticide mobility.

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Table 1. Vapor and Metabolic Loss of Butralin and Trifluralin from Matapeake Silt Loam (10).<sup>a</sup>

| Week   | Trapped <sup>14</sup> C as % of total applied |                               |       |              |                               |       |
|--------|-----------------------------------------------|-------------------------------|-------|--------------|-------------------------------|-------|
|        | Butralin                                      |                               |       | Trifluralin  |                               |       |
|        | Plugs                                         | <sup>14</sup> CO <sub>2</sub> | Total | Plugs        | <sup>14</sup> CO <sub>2</sub> | Total |
| 1      | 0.45<br>(82)                                  | 0.10<br>(18)                  | 0.55  | 4.42<br>(95) | 0.18<br>(5)                   | 4.60  |
| 2      | 0.43<br>(84)                                  | 0.08<br>(16)                  | 0.51  | 0.86<br>(81) | 0.20<br>(19)                  | 1.06  |
| 3      | 0.37<br>(72)                                  | 0.15<br>(28)                  | 0.52  | 1.16<br>(69) | 0.49<br>(31)                  | 1.65  |
| Totals | 1.25                                          | 0.33                          | 1.58  | 6.44         | 0.87                          | 7.31  |

<sup>a</sup> Since there was no difference in the amount of <sup>14</sup>C lost as volatile products in the light or dark, the values presented represent averages of four replications. Numbers in parentheses indicate percent <sup>14</sup>C appearing in plugs and CO<sub>2</sub>.

Table 2. Gas-liquid chromatographic determination of insecticide residues found in various parts of soybean plants exposed to soil treated with  $^{14}\text{C}$ -DDT, -dieldrin, -endrin, or -heptachlor (12).

| Insecticide<br>residues | Source of contamination |      |       |               |        |       |
|-------------------------|-------------------------|------|-------|---------------|--------|-------|
|                         | Vapor sorption          |      |       | Root sorption |        |       |
|                         | Leaves                  | Stem | Seeds | Leaves        | Stem   | Seeds |
| ppm                     |                         |      |       |               |        |       |
| <u>DDT</u>              |                         |      |       |               |        |       |
| DDT                     | 10.35                   | 0.78 | 0.00  | 0.01          | 0.00   | 0.00  |
| DDE                     | 1.97                    | 0.08 | 0.00  | 0.01          | Trace  | 0.00  |
| DDD                     | 0.11                    | 0.03 | 0.00  | 0.00          | 0.00   | 0.00  |
| Total                   | 12.43                   | 0.89 | 0.00  | 0.02          | Trace  | 0.00  |
| <u>Dieldrin</u>         |                         |      |       |               |        |       |
| Dieldrin                | 18.87                   | 2.11 | 0.73  | 6.43          | 104.91 | 0.71  |
| <u>Endrin</u>           |                         |      |       |               |        |       |
| Endrin                  | 12.28                   | 0.78 | 0.31  | 23.86         | 173.99 | 0.09  |
| Endrin ketone           | -                       | -    | 0.01  | -             | -      | 0.15  |
| Total                   | 12.28                   | 0.78 | 0.32  | 23.86         | 173.99 | 0.24  |
| <u>Heptachlor</u>       |                         |      |       |               |        |       |
| Heptachlor              | 0.42                    | 0.60 | 0.08  | 0.10          | 3.16   | 0.02  |
| Hydroxchlordene         | 0.10                    | 0.03 | 0.00  | 0.87          | 0.85   | 0.04  |
| Heptachlor epoxide      | 0.44                    | 0.21 | 0.25  | 1.37          | 27.33  | 0.34  |
| Total                   | 0.96                    | 0.84 | 0.33  | 2.34          | 31.34  | 0.40  |

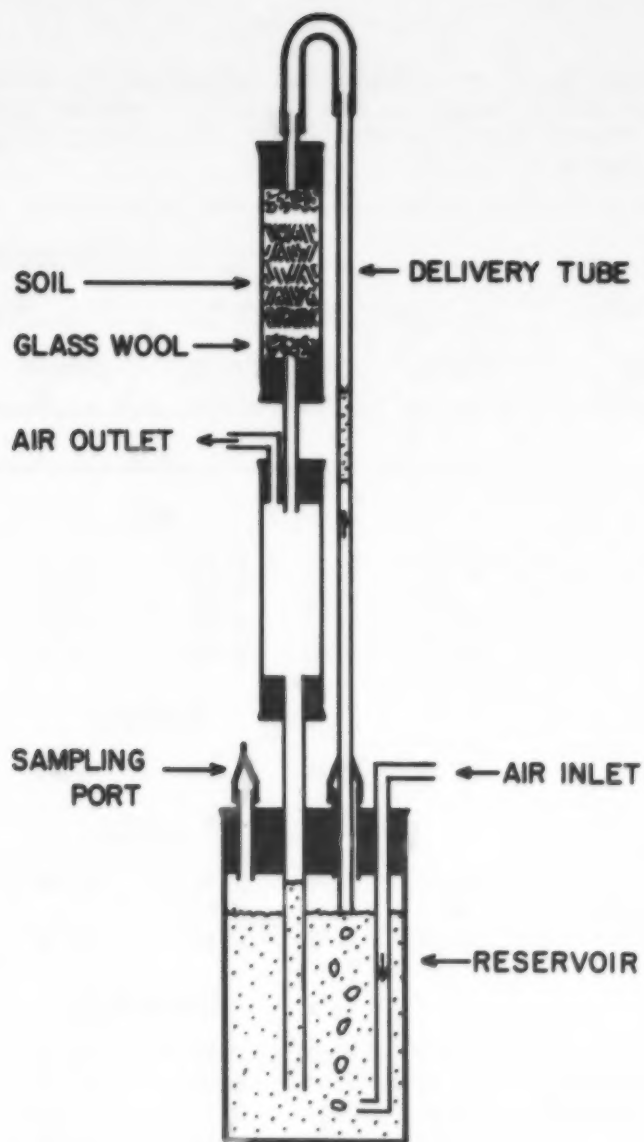


Figure 1. Diagram of soil perfusion unit (2).



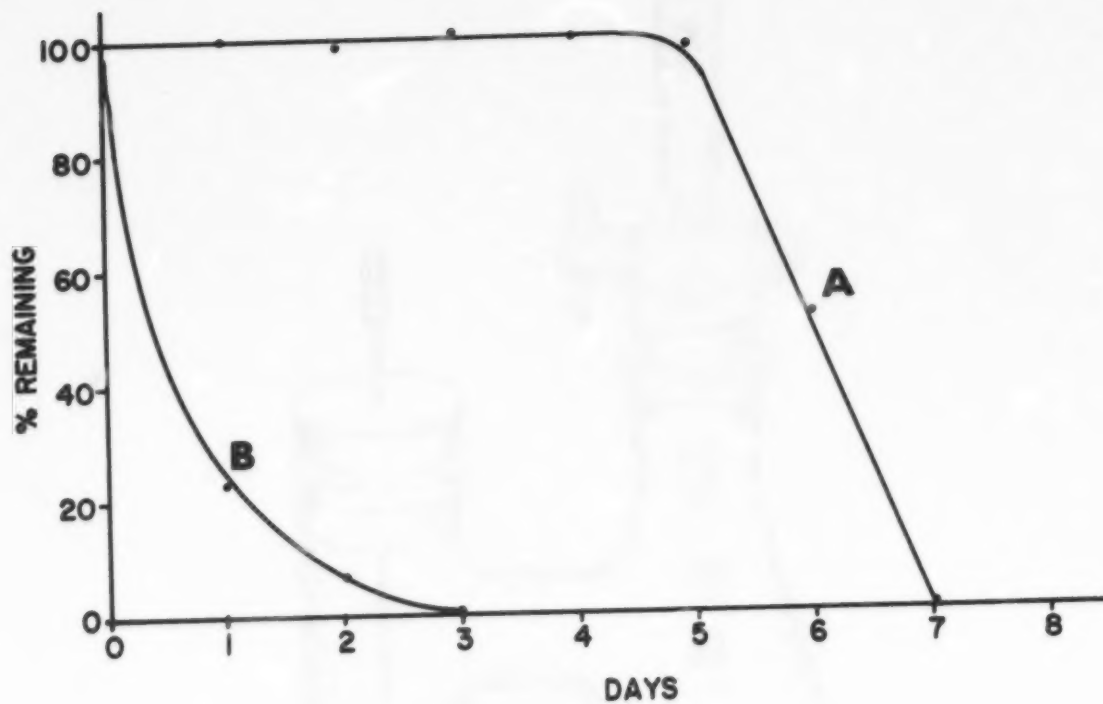


Figure 2. Microbial degradation of dalapon in (A) an untreated soil perfused with an aqueous solution of dalapon; and (B) the same soil, re-perfused with a second supply of aqueous dalapon (2).

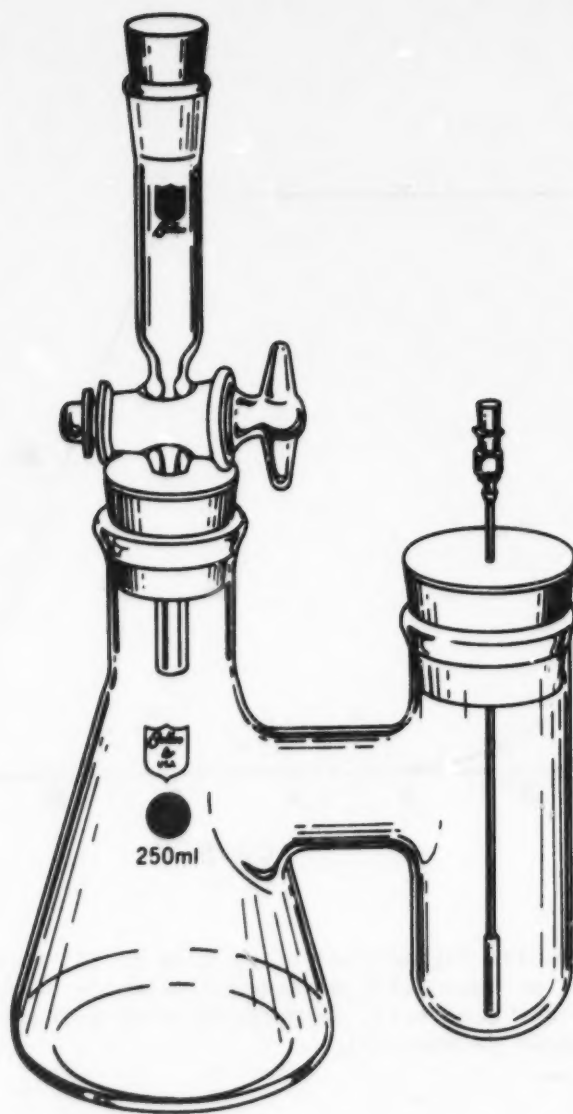


Figure 3. Soil biometer flask (9).

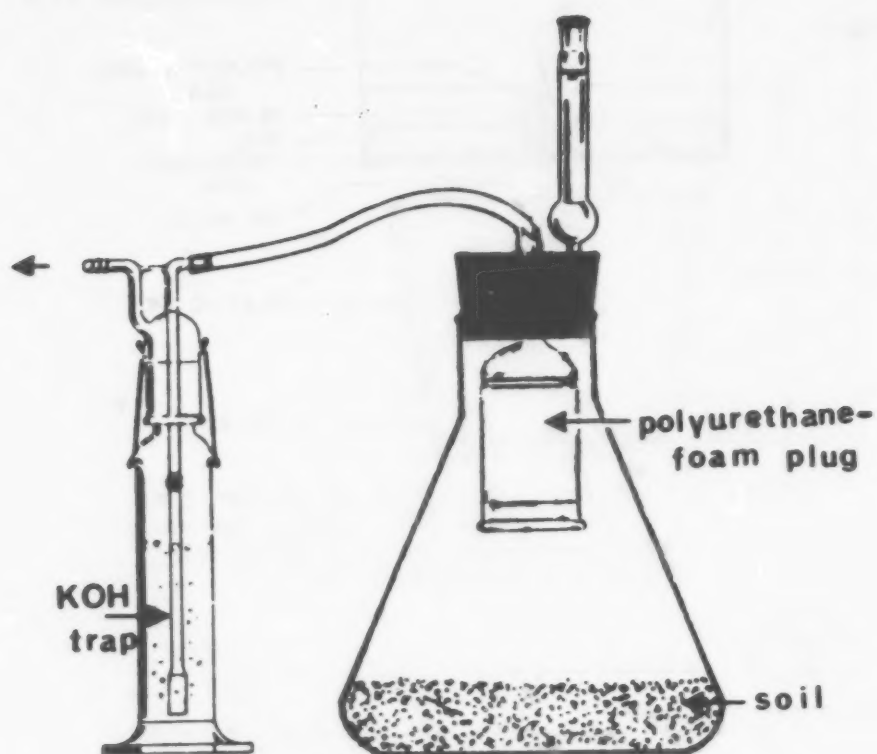


Figure 4. Diagram of system designed to measure volatilization and metabolism in or on soils (10).





## COMETABOLISM OF FOREIGN COMPOUNDS

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A characteristic feature of the most part of present investigations on microbial degradation of xenobiotic compounds is the absence of certain idea about ways of practical application of microbiological methods. Analysis of up-to-date situation shows a distinct discrepancy between laboratory science trends and conceivable technology of practical realization of obtained results.

The main attention of the scientists is paid to isolation of microorganisms capable to use xenobiotics as a sole carbon sources under traditional laboratory conditions - pure culture, high aeration, optimal temperature and so on.

These "classical" approaches resulted many times in disappointments at the attempts to apply cultures, obtained at the laboratories for degradation of xenobiotic in natural habitats.

So, Andersen tried to use a fungal culture *Mucor alternans*, capable to transform DDT into water-soluble products under laboratory conditions for degradation of this pesticide in soil. He did not receive desirable result. The explanation was that natural soil microflora interfered with function of introduced culture.

We tried to introduce the biomass of cultures degrading ordram into a water of a natural reservoirs, contaminated by this herbicide. The applied cultures were *Pseudomonas aeruginosa* and *Bacillus* sp. isolated from water habitats, contaminated by ordram a year before. In both of the experiments the introduced cultures disappeared completely in 24 hours or near that.

According to prof. Zwjaguinzev, bacterial cultures should be introduced into the soil not less than 1 t per hectare to obtain a positive effect in xenobiotic content decrease.

The positive experience known concerns to hydrocarbon decomposing microorganisms. The experiments on degradation of petroleum products, contaminating soils were carried out by american scientists and are well known. It should be mentioned, however, that was the most simple case, because petroleum hydrocarbons are oxidized by many naturally occurring microorganisms, and besides, the inoculums of microbial mass were rather heavy.

Thus, taking into account these considerations, one can conclude, that microorganisms, obtained at the laboratories, can be applied in the first line in so called intensive methods suggesting the construction of special installations of industrial type, where the microorganisms could be applied as a components of active sludges or in some immobilized (fixed up) form.

For degradation of xenobiotics, accumulated in the biosphere at the vast aerias of soils or waters, one needs another approaches-extensive ones, which don't requirer creating of complicated technological schemes of industrial scale. The introduction of foreign microorganisms into soils or water is hardly suitable way to solve this problem. The required quantities of microbial mass should be too great and the effect is too transient. To

obtain a stable permanent effect, one has to solve quite another problem, in fact creating of new, artificial ecosystem. That's why from our point of view, the more proper approach to extensive methods of xenobiotics degradation is a mobilization of capacities of natural microflora.

There are at least two ways to do that - the first one - supplying of natural microflora by N and P sources (this was demonstrated by american authors in case of petroleum contamination of the soil) and the second - method of cometabolism.

These approaches make possible extensive methods of microbiological degradation of xenobiotics in the environment.

Study of cooxidation of aromatic hydrocarbons and heterocyclic compounds by microorganisms at the expense of other compounds - hydrocarbons, carbohydrates etc. has drawn the attention of microbiologists to the regulations of interaction between microorganisms and some other substrates (Horvath, 1972; Skryabin, Golovleva, 1976). It is stated that fermentative conversions of many organic substances are closely connected or even depend on oxidation of other compounds - cosubstrates. This dependence is generally called cometabolism.

There is no strict definition of the notion "cometabolism" and different authors treat it differently.

Some investigators-specialists in the field of soil microbiology-Alexander, Horvath consider cometabolism to be transformation processes i.e. partial conversion carried out by microorganisms, growing or grown on substrates inducing synthesis of transforming fermentative system (Horvath, Alexander, 1970; 1970a). For instance, Horvath and Alexander gave as an example of cometabolism the description of transformation of m-chlorobenzoic

acid in 4-chlorocatechol by cell *Arthrobacter* sp. grown on the medium with benzoic acid. In this case the substrate was oxidised more intensively and without lag-phase. (Horvath, Alexander, 1970).

We consider cometabolism to be the processes of fermentative conversion of organic compounds which are carried out by microorganisms only in conjugation with the use of additional substrates. Cometabolism reaction of some substrate exhibits itself only in the presence of cosubstrate of certain structure and in case it is metabolised. Close interrelation between metabolism of the two substrates, dependence of cometabolism process on the nature of cosubstrate are, in our opinion, the characteristic and distinctive features of cometabolism, representing biological specificity of this phenomenon. The best known are the cometabolism processes of foreign compounds-xenobiotics, though there are also the examples of cometabolism of natural compounds for instance steroids and terpenes as well as such substrates as xylose, widely spread in nature and easily metabolized (Yoshitake et al., 1971).

Our investigations prove that conversions of many xenobiotics are possible only under cometabolism conditions.

Nowadays the following reactions carried out under the cometabolism conditions are described.

- 1) Oxidation of methyl groups of n-alkanes (Leadbetter, Foster, 1960);
- 2) Oxidation of methyl groups of aromatic and heterocyclic compounds (Raymond et al., 1976; Skryabin, Golovleva, 1976).
- 3) Oxidation of cycloalkanes (Ooyama, Foster, 1965).
- 4) Hydroxylation of aromatic ring, hydroxylation of steroids (Vesina et al., 1969);

- 5) Acetylation of aminogroups (Golovleva et al., 1975);
- 6) Co-reduction (Noma et al., 1973; 1974);
- 7) Cyclization of aliphatic radical (Skryabin et al., 1974),

Partial and full degradation of such recalcitrant pesticides as 2,3,6-TBA, 2,4,5-T acid, DDT has been described. In our laboratory we have completely decomposed herbicides alvison-8 and ordrame under cometabolism conditions. The latter is resistant herbicide and until recently there was no data about its degradation.

Consequently, both the processes of xenobiotic transformation and their full degradation can occur under the cometabolism conditions.

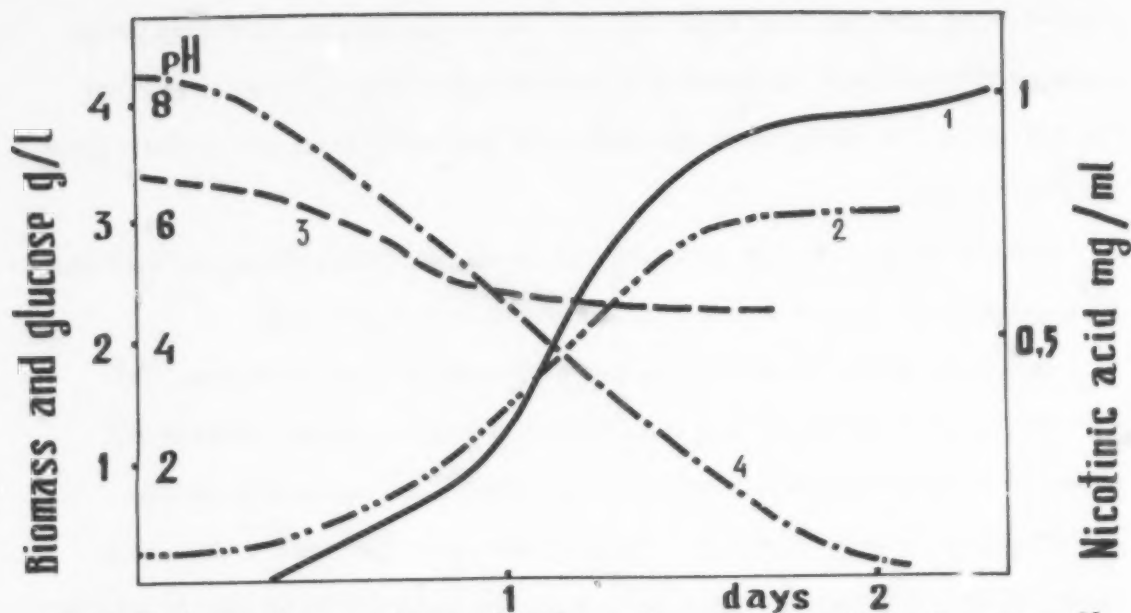
Let us consider in detail the types of cometabolism reactions. The culture *Nocardia corallina* I A transformed isomeric xylenes, substituted toluenes, alkylpyridines, cresols only in the process of growth on the variety of additional substrates fig 1. Degradation of alvison-8 also took place during the growth of this culture on the medium with octane or glucose fig.2. Degradation of herbicide ordram was also carried out under the growth of *Bacillus* sp.21 on the medium with ethanol fig.3.

At the same time there exist processes which take place not during the growth but in the process of cosubstrate metabolism.

Oxidation of p-xylene and 3-methylpyridine by *Nocardia corallina* I A was performed conjugated with xylose conversion to xylonic acid fig.4. Culture growth on the medium with xylose was not observed, i.e. in this case transformation of foreign compound took place together with cosubstrate transformation.

Degradation of herbicide alvison-8 *Pseudomonas diminuta* and *Pseudomonas putida* was also carried out only in the process of co-substrate metabolism





### 3-Methylpyridine oxidation by *Nocardia corallina* 1A under growth on glucose

1 - concentr. of nicotinic acid  
2 - culture growth

3 - pH  
4 - glucose decrease

Fig.1. 3-Methylpyridine oxidation by *Nocardia corallina* 1A under growth on glucose.

1 - concentr. of nicotinic acid, 2 - culture growth, 3-pH,  
4- glucose decrease.

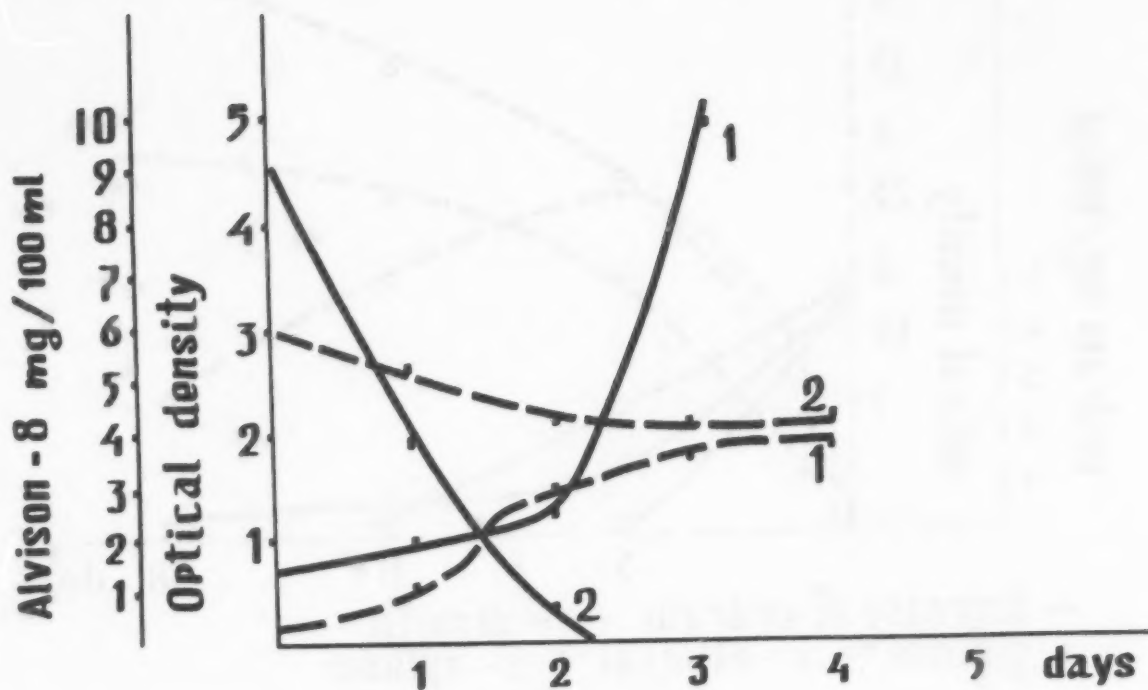


Fig.2. Growth of *Nocardia corollina* (-) and *Pseudomonas aeruginosa* B-12 (---) on glucose 1. Decrease of alvison -8-2.

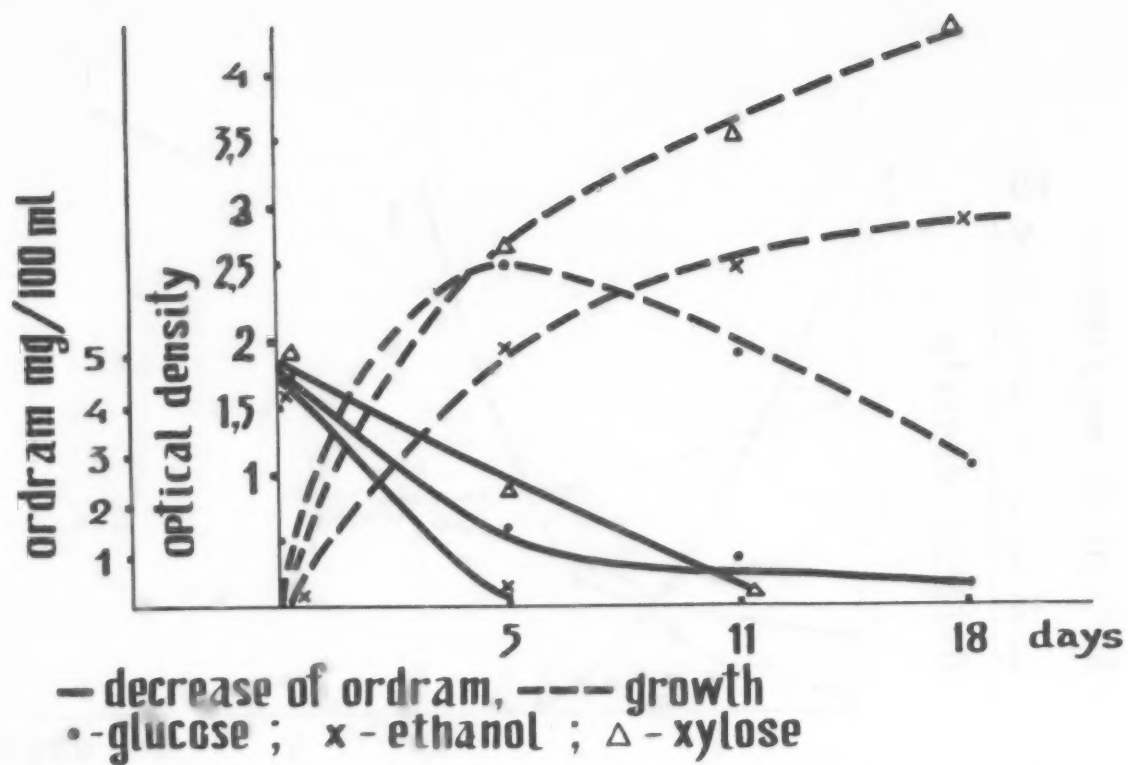


Fig.3. Ordram degradation by *Bacillus* sp 21R under growth on different substrates.

- decrease of ordram, - - - growth, o - glucose, x - ethanol,  
 - xylose.

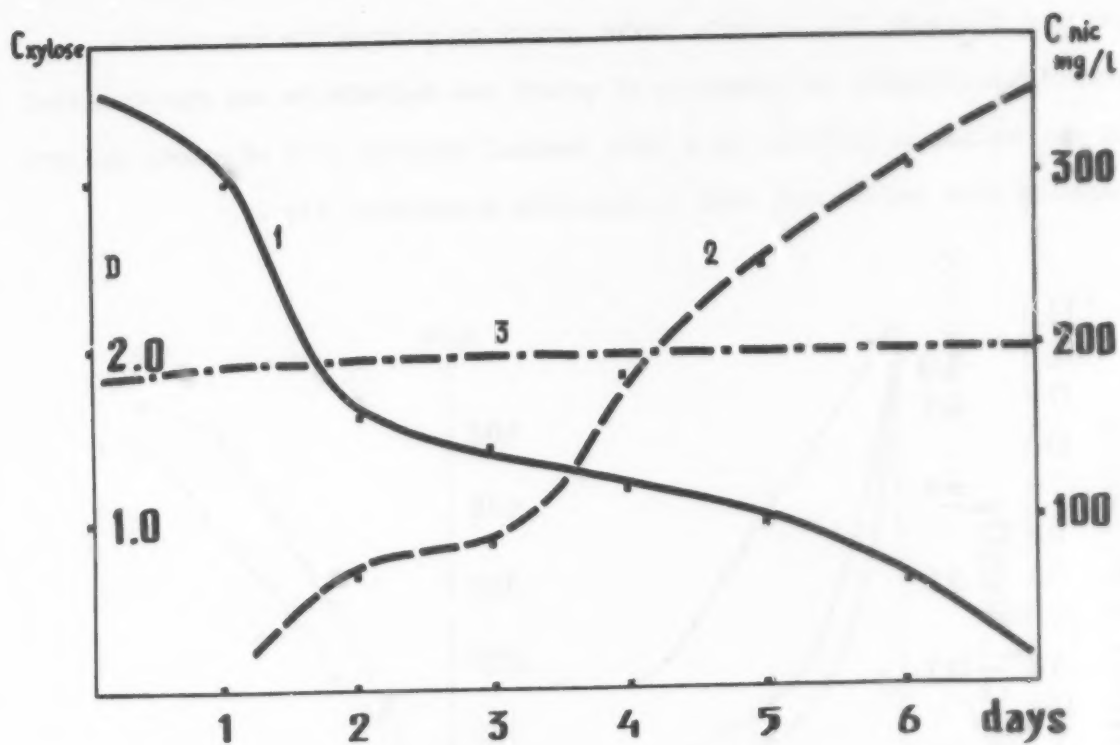


Fig.4. Transformation of 3-methylpyridine by *Nocardia corallina* 1A conjugated with xylose transformation.

1 - xylose concentration; 2 - nicotinic acid concentration,  
3 - optical density.

fig.5. None of the active cosubstrates served as a growth substrate for these cultures even after the addition of growth factors though all of them were actively oxidized by washed cells in Varburg apparatus.

It should be noted that even alvison degradation was carried out in the process of growth (for example, under growth on glucose for the culture *Nocardia corallina*) the intensity of growth and degradation was characterised by the inverse proportion. As a rule, maximal specific rate of growth did not coincide with the maximal rate of herbicide degradation fig 2 .

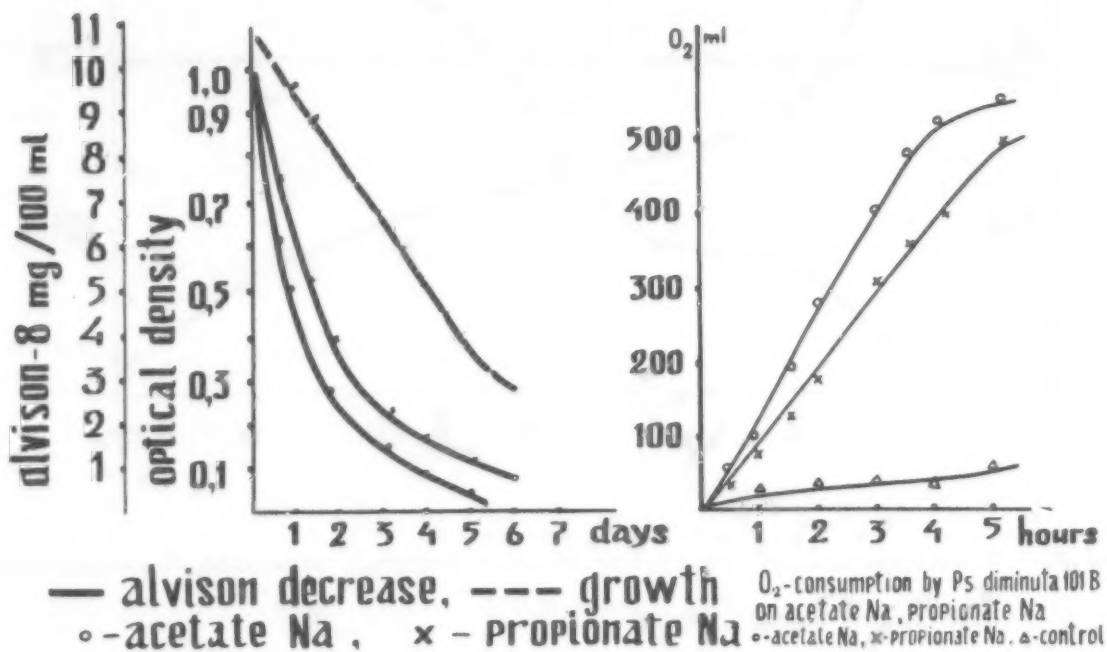


Fig. 5. Alvison-8 degradation by *Ps. diminuta* conjugated with co-substrates metabolism

- decrease of alvison, - - growth, o - acetate, x - propionate.

O<sub>2</sub> - consumption by *Ps. diminuta* 101B on acetate (o), propionate (x),

- control.



The analysis of the presented data allows to assume that the mechanisms of co-oxidation of different substrates by various cultures differ in some characteristic details each other. These mechanisms depend, in part, on the ability of microorganisms to metabolise various carbon compounds and to use them as a growth substrate as well as, probably, on the specificities of catabolism of co-substrates with different structure. However there can be noticed a general principle of cometabolism processes - the processes of degradation carried out under the co-oxidation conditions are the most effective in the presence of co-substrates which are intensively metabolized but are unable to maintain intensive growth of microorganisms. Consequently it is possible to speak about four types of cometabolisms:

- 1) transformation of foreign compound in the process of microorganism growth on the expense of co-substrate;
- 2) xenobiotic transformation under the co-substrate transformation; in this case the co-substrate is not the source of carbon;
- 3) degradation of the main substrate under the microbial growth at the expense of co-substrate;
- 4) xenobiotic degradation under the co-substrate transformation.

In spite of the obvious and very close dependence of the main substrate transformation on the nature of co-substrate the character of this relation is not clarified yet. As I have already mentioned above, our experiments with introduction of microorganisms into natural water reservoirs did not give positive results.

However, the degradation of herbicides was significantly accelerated after introducing of co-substrates. So, analysis of 2,4-D dynamics in waste waters of rice fields has shown that 2,4-D disappeared more quickly if

propionate was used as co-substrate. In this case the herbicide was not detected in the water in 3 days, at the same time about 25% of initial 2,4-D was present in control experiments (without propionate) fig.6.

Similar results were obtained in experiments of this year in Moscow region with ordram degradation. Addition of cosubstrate-ethanol to a water reservoir accelerated ordram degradation in comparison to control (without cosubstrate).

The study of cometabolism is at the first stage of its development. There is no doubt that the knowledge of regularities of interrelation between microorganisms and several substrates is not only practically but also theoretically important, i.e. the importance of the study of cometabolism as biological phenomenon is beyond doubt.

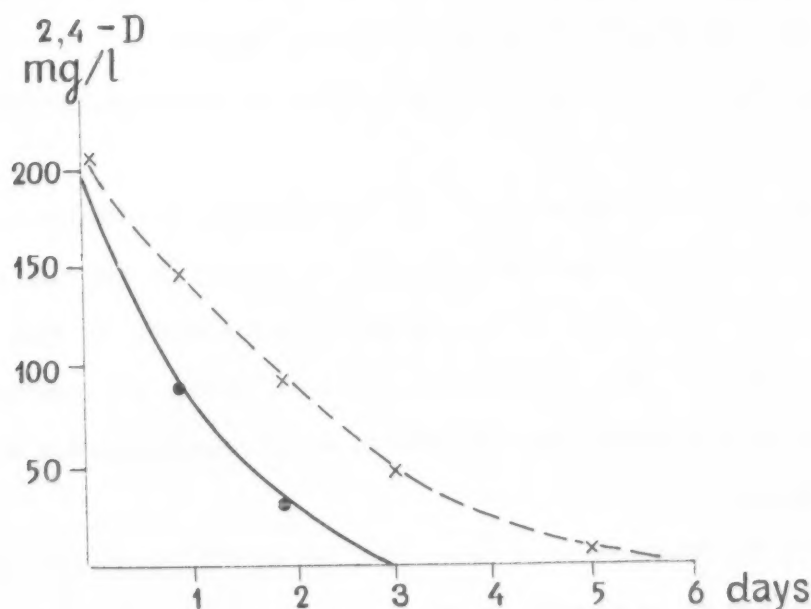


Fig.6. Cometabolism 2,4-D with (-) and without (- - -) propionate.

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ON THE ESTIMATION OF THE ANTHROPOGENIC POLLUTION EFFECT  
ON THE FUNCTIONAL STATE OF THE SOIL MICROFLORA

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The biosphere is the ecological system in which a variety of organisms and their associations are in a definite interaction with the environment. Ever-increasing anthropogenic activity results in the accumulation in the biosphere of stable compounds which can significantly change the living conditions and, consequently, the reactions determining interactions between organisms and the environment.

Among all the geophysical media, soil is subjected to the greatest anthropogenic action and is the most dangerous link in the circulation of industrial and agricultural toxic materials. Microorganisms play a leading part in the biogenic migration and transformation of organic and mineral substances in soil. Biotransformation accomplished by the soil microflora involves a great quantity of chemical elements amounting to millions and billions of tons. The number and amount of substances involved in biotransformation and biogenic migration increase with the

development of industry and the increase in application of chemicals in agriculture.

The interaction of microorganisms with foreign for the biosphere substances is intensively investigated, mainly relative to the ability of microorganisms to decompose synthetic compounds. As for the effect of industrial and agricultural toxic materials upon the soil microflora, it is investigated very poorly. Data on this problem available in literature are very contradictory.

Due to the fact that the soil cover together with its micro-world plays a role of the universal biotransformer of organic and mineral substances, and that the accumulation of toxicants in soil presents danger for the vital activity of the soil microflora and transformation processes fulfilled by it, there arose a problem of assessing and forecasting the state of soil which is one of the main components of the ecosystem.

The integral index of the soil state is its biological activity [1]. The biological activity of soil is a concept reflecting the whole complex of biotransformation processes taking place in soil. One of the main indexes of the biological activity of soil is the enzymic activity [2, 3, 4]. There are many enzymes initiating the biotransformation processes in soil. However, not all of them can be used for the assessment of the functional state of microorganisms because their role in the processes of the vital activity of cells is different.



An essential manifestation of the vital activity is metabolism, that is, a complex of processes directed to the reproduction of living substance. The energy required for this is released by the oxidation-reduction processes. Enzymic systems catalyzing the transport of electrons are very complicated and act as highly organized complexes.

Oxidoreductases are very numerous, but not a single full biological oxidation process occurs without participation of dehydrogenases [5]. A universal role of dehydrogenases in the biotransformation processes accomplished by living cells is explained by their ability to induce the transport of electrons both under aerobic and anaerobic conditions using various organic and mineral components of soil as an acceptor of hydrogen [6]. Thus, co-oxidation is one of the most important manifestations of the vital activity of microorganisms in which dehydrogenases play an essential role.

Investigation of a number of indexes of the biological activity of soils shows a good correlation of the dehydrogenase activity with the proteolytic, nitrifying, respiratory activity and absorption of oxygen by soil [7,8].

According to data obtained by many authors, the dehydrogenase activity depends on all the ecological factors in soil which determine the quantitative and qualitative composition of the soil microflora and reflect the level of its vital activity and the intensity of biotransformation processes in soil [9].

Data obtained by many authors show that the dehydrogenase activity presents a sensitive index of the total susceptibility of

the microflora of soils and active silts to chemical substances toxic for main reactions of metabolism [10, 11, 12, 13].

Based on all the said above, the dehydrogenase activity was chosen by us as a criterion for evaluating the effect of industrial and agricultural toxicants on the biological activity of the soil microflora.

To determine the dehydrogenase activity soil samples were taken from model experiments carried out in various types of soil in agricultural and industrial regions. The soil samples had various residues of the sum of  $\alpha$ ,  $\gamma$ -hexachlorocyclohexane, DDT and its metabolites and various amounts of the sum of heavy metals: lead, chromium, nickel, vanadium, copper. The dehydrogenase activity was determined in air-dried soil samples by the photolorimetric method from the amount of formazan formed by the reduction of triphenyltetrazolium using Lenhard's method modified by Ross. The results of the dehydrogenase activity determination were expressed as microliters of hydrogen, knowing that the formation of 1 mg of formazan requires 150.35 microliters of hydrogen. Analysis of the contents of  $\alpha$ ,  $\gamma$ -hexachlorocyclohexane, DDT and its metabolites in soil samples was made by the gas-liquid chromatography technique. Analysis of the contents of heavy metals in soil samples was made by the spectral method.

All the analyzed soil samples without addition of exogenous substrates and coenzymes were characterized by the dehydrogenase activity. When investigating the dehydrogenase activity depending on the incubation time, the short-period stable auto-oscillations

of activity were found under invariable experimental conditions (Fig. 1).

Methods for the dehydrogenase activity determination based upon one definite period of soil sample incubation give the state of microflora only during this period of time but do not characterize its general functional state. Thus, for example, determinations of the dehydrogenase activity in soils with relatively large and small residues of chloroorganic pesticides carried out by the above methods either do not show any difference in the microflora activity (Fig. 1 a, c, d) or give contradictory results (Fig. 1 b) for the first 24 hours of incubation. And only longer observations reveal that the functional activity of the microflora in soils with high contents of toxicants is lower than that in a relatively clean samples.

Taking into account auto-oscillations of the dehydrogenase activity and contradictions of its single measurements, we think that it is reasonable to evaluate the biological activity of the soil microflora from the dynamics of the dehydration process.

The short-period autooscillations of the dehydrogenase activity found by us were of a methodical value. Due to this, we began to estimate the state of microflora from the data of the dehydrogenase activity observations averaged over 10 days.

Investigations of the dynamics of the dehydration process in soils of agricultural regions with various residues of chloroorganic pesticides show that the average level of the dehydrogenase activity in soils with large contents of toxicants is lower than

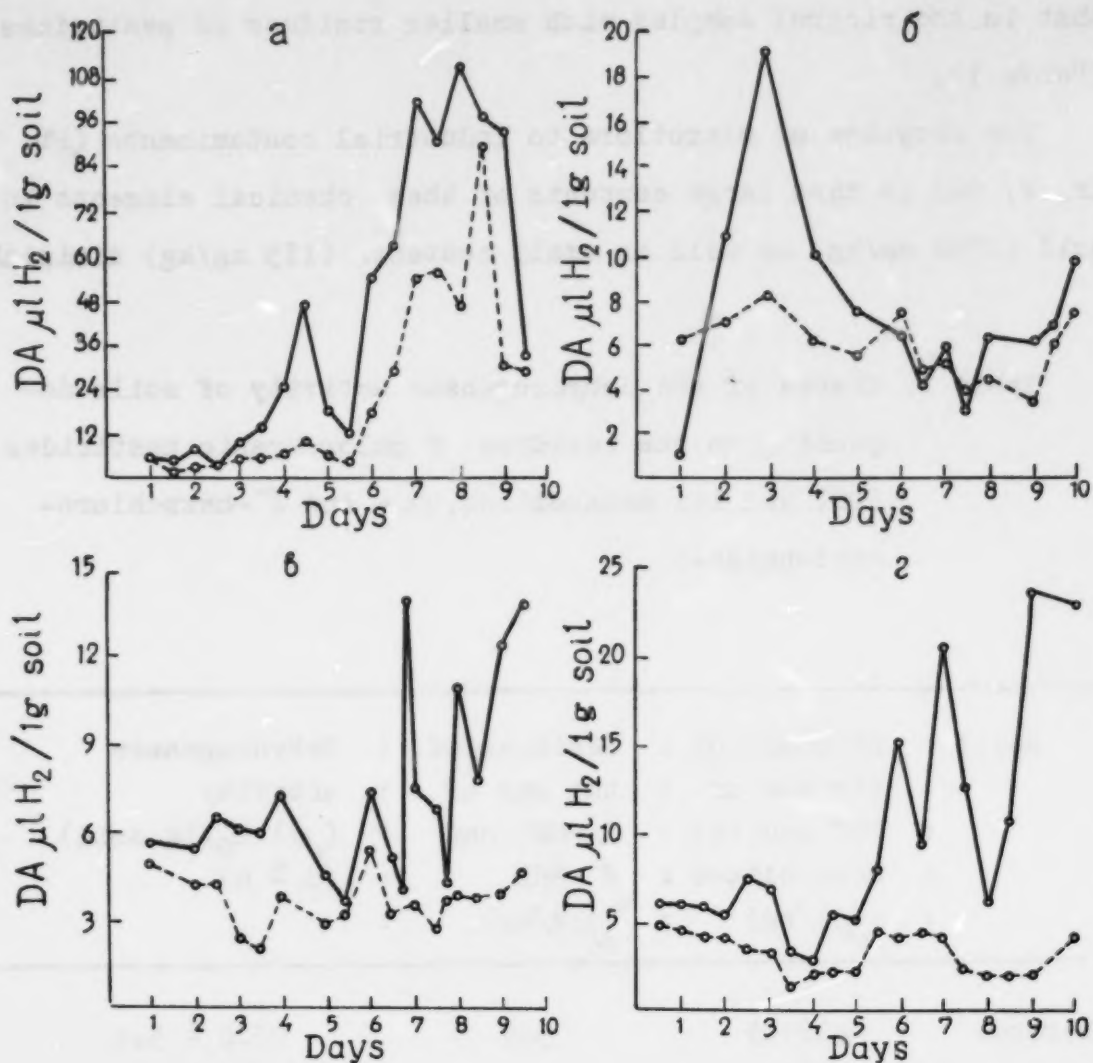


**Fig. I.** Change of the dehydrogenase activity of the microflora in soils having various residues of pesticides (the sum of DDT and its metabolites,  $\alpha$ - and  $\delta$ -hexachlorocyclohexane) depending on the incubation time.

—○—○— soils with relatively low residue of pesticides;  
 - - -○- soils with relatively high residue of pesticides.



that in the control samples with smaller residues of pesticides (Table I).

The response of microflora to industrial contaminants (Pb, Ni, Cr, V, Cu) is that large contents of these chemical elements in soil (2760 mg/kg) as well as small contents (115 mg/kg) diminish

Table I. Change of the dehydrogenase activity of soils depending on the residues of chlororganic pesticides (DDT and its metabolites,  $\alpha$ - and  $\delta$ -hexachloro-cyclohexane)

| Soils :    | Residues of :   | Residues of :       | Dehydrogenase                      |
|------------|-----------------|---------------------|------------------------------------|
| :          | the sum of :    | the sum of :        | activity                           |
| :          | DDT and its :   | $\alpha$ -BHC and : | ( $\mu$ l H <sub>2</sub> /Ig soil) |
| :          | metabolites :   | $\delta$ -BHC :     | ( $M \pm m$ )                      |
| :          | ( $\mu$ g/kg) : | ( $\mu$ g/kg) :     | :                                  |
| Sierozem   | 22403           | 327                 | 25.0 $\pm$ 5.4                     |
|            | 627             | 12                  | 49.3 $\pm$ 9.8                     |
| Ordinary   | 1964            | -                   | 27.1 $\pm$ 9.4                     |
| chernozem  | 54              | -                   | 52.0 $\pm$ 13.7                    |
| Calcareous | 1081            | 6                   | 3.1 $\pm$ 0.3                      |
| chernozem  | 52              | 5                   | 11.6 $\pm$ 2.6                     |



the dehydrogenase activity (Table 2). And only in a definite concentration range (162-586 mg/kg) the dehydration processes are intensive.

The toxic effect of high concentrations of heavy metals in soils of industrial regions is greater than that of pesticides.

Decrease in the dehydrogenase activity in soils with high contents of toxicants may be one of the reasons of decreasing the rates of their biotransformation and this results in increase of the time periods of their toxic effect. We made an attempt to assess the toxicity of soils with high contents of toxicants and low dehydrogenase activity from the germination of clover and bar-

Table 2. Change of the dehydrogenase activity of soils depending on the contents of the sum of heavy metals (Pb, Ni, Cr, V, Cu)

| The sum of heavy metals<br>(mg/kg) | Dehydrogenase activity<br>( $\mu$ l H <sub>2</sub> /1 g soil)<br>(M $\pm$ m) |
|------------------------------------|------------------------------------------------------------------------------|
| 2760                               | 3.5 $\pm$ 0.3                                                                |
| 586                                | 23.4 $\pm$ 3.1                                                               |
| 162                                | 33.2 $\pm$ 4.6                                                               |
| 115                                | 3.4 $\pm$ 0.4                                                                |

ley seeds. The germination of clover and barley seeds (during 15 days at temperatures of 20-25°C and 60% of total moisture capacity) was the better, the higher was the dehydrogenase activity. In soils with the dehydrogenase activity of about unity, the ger-

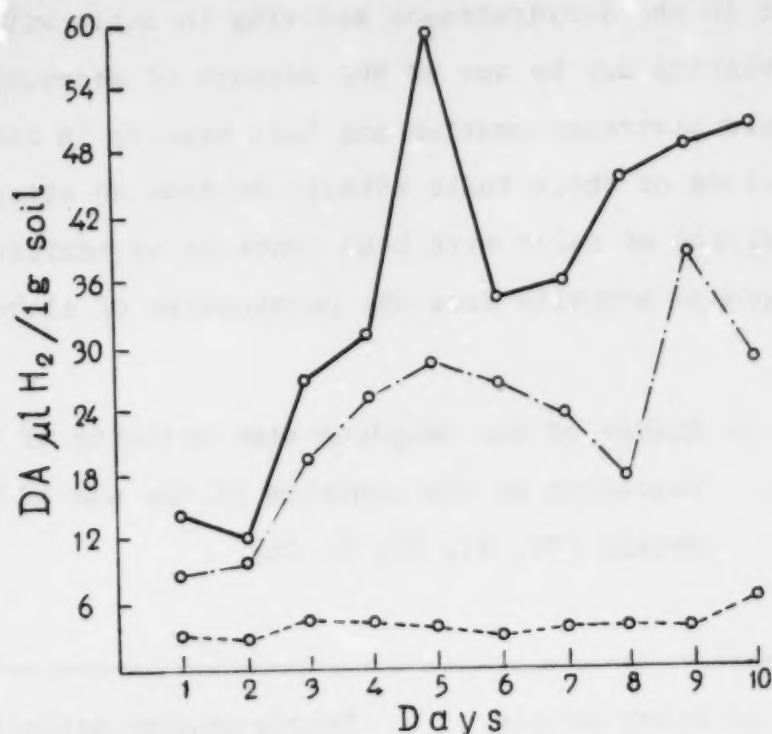


**Fig. 2.** Change of the dehydrogenase activity of the microflora in soils with various contents of heavy metals (Pb, Cr, V, Ni, Cu) depending on the incubation time.

- o ——— o - total amount of metals (162 mg/kg)
- o — . — o - total amount of metals (586 mg/kg)
- o - - - - o - total amount of metals (2760 mg/kg)

mination of seeds either did not occur at all or was retarded.

Recognizing the similarity between the action of toxicants on the living cell one should recognize the similarity between mechanisms of their action as well.

The data presented in this paper indicate that the toxic effect of chlororganic pesticides on the soil microflora may be accounted for by the disturbance of the dehydration processes which are of energetical value for the cell. And the decrease in the dehydrogenase activity may lead to a decrease in the biotransformation processes associated with it.

Further investigation of the chosen criterion seems to us perspective not only in the practical aspect but also in the theoretical one.

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## TRANSFORMATION AND TRANSPORT PROCESSES IN AQUATIC SYSTEMS

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Dynamics of transformation and transport are described in terms of their controlling environmental parameters. Recent advances in our ability to mathematically describe the rate and extent of microbiological, chemical, and physical processes are discussed and data are presented to illustrate interrelationships between these processes.

Microbiological rates have generally been modeled using Monod kinetics. This kinetic model (1) is described and the effect of isolation and high substrate concentration on the growth constants demonstrated (2). When substrate concentrations are low as in the case of insoluble compounds like many pesticides, the Monod expression reduces to second-order rate expression (3,4). Studies of malathion degradation by bacteria gave results that agreed within a factor of two when the second-order rate constant was measured directly or calculated from Monod constants. More recent studies (5,6) have compared data from chemostats, flasks, and a simulated stream system which incorporate both chemical and microbial degradation.

Partitioning of stable insoluble pesticides between water and microorganisms has recently been given greater attention. In most cases this phenomenon has been found to be rapid, reversible, and adequately described by a Freundlich isotherm or partition coefficient (3,7,8). However, Sugiura *et al.* (9) have reported a two-step process for accumulation of BHC isomers. Some implications of partitioning have been shown by preferential accumulation in bacteria of the more water insoluble components of toxaphene (10).

Chemical reactions in water can occur by many different mechanisms, some of which have been described by Wolfe *et al.* (11). However, reaction of pesticides with water (hydrolysis) is one of the most important chemical transformation mechanisms in aquatic systems. It has been shown that the pH dependence

of these reaction rates is predictable and that the half-life is a poor indicator of rate unless reactant concentrations are specified. Recent detailed kinetic studies on malathion (12) and cyanazine (13) have quantified the effect of temperature and pH over a wide range. Malathion studies have demonstrated the effect that temperature (12) and pathway (3) can have on transformation products. The use of structure activity relationships to predict hydrolytic rate constants has been applied to the case of 2,4-D esters (14) in considering competition between hydrolysis, photolysis, and volatility.

The effect of a rapid pre-equilibration step on rate processes can be described by an equation of the form

$$-\frac{d[P]_T}{dt} = \frac{k[P]_T}{1 + K[A]} \quad (1)$$

where  $[P]_T$  = concentration of total pesticide in the system  
 $K$  = equilibrium constant (partition coefficient)  
 $k$  = pseudo-first-order rate constant  
 $[A]$  = concentration of sorbent (solvent) in the system.

Effects of sediment partitioning on hydrolytic half-life (15) and volatilization rate are demonstrated by data on pesticides and PCBs. Singmaster (16) has also applied eq. 1 to DDT hydrolysis in the presence of a partitioning solvent.

Evidence is also presented to support the possible importance of other chemical reactions as indicated by abiotic methylation of mercury (17), N-nitrosation of atrazine (18), and degradation of methoxychlor.

Photochemical transformations are described in terms of three different processes (11,19): direct photolysis, sensitized photolysis, and indirect photolysis. Kinetics of direct and sensitized pesticide photolysis have been studied for a number of pesticides in water (11,14,19,20).

Under most environmental conditions the pesticide absorbs only a small fraction of the light, and the rate law is first-order in pesticide and a function of light intensity. However, light intensity in aquatic systems is a function of latitude, time of day, season, water absorbance, and depth. A recently completed computer program (19) for direct photolysis rates couples these properties with the spectrum of the pesticide and its quantum yield. Data are presented which show the effect of latitude on photolysis rates of carbaryl and trifluralin. Agreement between computed and observed half-lives of several pesticides is discussed.

Photolysis rate of parathion in natural waters is approximately proportional to water absorbance and independent of the water source. In this case reaction apparently occurs by energy transfer and paraoxon and P-nitrophenol are the major products.

Physical transport from water to air is a pathway that has received little attention and its importance for most pollutants is poorly understood. A method (21) for the reaeration capacity of streams is suggested as an approach for volatilization of organics (22). Studies of this type carried out with PCB's in our laboratory are presented. Another technique based on Henry's law and average volatilization rates (23,24) of water has been applied to DDT (16), 2,4-D esters (14), and a number of other organic compounds (25).

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ESTIMATION OF ORGANOCHLORINE PESTICIDE LOSS IN SURFACE  
RUNOFF WATERS

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Pesticide migration in water is one of the major pathways of their transport in the environment.

Surface runoff water which occurs at the watershed as the result of snowmelt or rainfall causes pesticide removal from the watershed area (agricultural lands and forests) and their entering rivers and basins.

Investigations showed that surface runoff from the watershed was the major source of river water pollution with pesticides.

In spring the channeled runoff of the most plain rivers of the Soviet Union is formed mainly by snowmelt waters from the watershed. It is over this period that one should expect the most pesticide removal from the watershed area and their entering river channels.

It is necessary to quantify pesticide loss in surface runoff waters from the watershed both when considering pesticide transport

in the environment as a whole and when predicting surface water pollution with pesticides.

The amount of pesticides entering the river network in surface runoff waters from the watershed depends on a number of factors, the major factors being pesticide solubility in water and conditions of water runoff from the watershed. It should be noted that according to the works by Nicholson [1], the amount of pesticides in runoff waters is affected by the time interval between the pesticide application and the first surface runoff.

We investigated the loss of organochlorine pesticides - DDT and  $\gamma$ -BHC in surface runoff waters over the period of spring flood and rainfall.

Pesticide loss in runoff waters in spring was studied at the natural river watersheds where pesticides had not been applied in the previous 5 years and at the experimental runoff plots when simulating pesticide fallout on the snow cover as well as the loss of pesticide residual amounts in runoff waters from these plots.

Pesticide loss in rain runoff waters due to the natural summer precipitation was studied at the experimental runoff plots installed at the natural river watershed.

Pesticide loss in surface runoff waters from the watershed was characterized quantitatively by the loss coefficient which was determined from the formula:

$$f = \frac{u}{N_1 + N_2}$$

where  $u$  is the amount of pesticides lost from the watershed (run-off plot);

$N_1$  is the amount of pesticides at the watershed (0-20 cm soil layer);

$N_2$  is the amount of pesticides in the watershed snow cover before the snowmelt - in spring;

or the amount of pesticides deposited with rain - in summer.

Pesticide loss in runoff waters over the period of spring flood was investigated at two watersheds in the Moskva-river basin: in its upper course and in one of its tributary. The first watershed area was 5000 km<sup>2</sup>, two thirds of this area being regulated by the storage reservoirs, and the second one was 800 km<sup>2</sup>. In spring the formation of river runoff at the first watershed occurs mainly due to snowmelt waters from the non-regulated part of the watershed. This fact was taken into account in the further calculations.

Water samples were collected every day at the terminal observation point of a given watershed and required hydrological observations were carried out. Using the data obtained we calculated the amount of pesticides ( $u$ ) lost from the watershed over the period of spring flood. The amount of pesticides in the watershed soils ( $N_1$ ) was determined by collecting soil samples (0-20 cm layer) with regard to their properties and species of crops at the agricultural lands. The amount of pesticides in the watershed snow cover ( $N_2$ ) was calculated from the results of snow survey and determination

of pesticide content in snow samples collected over the whole depth of snow cover.

The coefficients of pesticide loss in surface runoff waters calculated from the above formula were 0.06% and 0.09% at the first watershed and 0.3% and 0.1% at the second one for DDT and  $\gamma$ -BHC, respectively.

These results were obtained at the DDT and  $\gamma$ -BHC contents in soils from 5 to 60  $\mu\text{g/kg}$  and from 0.8 to 4  $\mu\text{g/kg}$ , respectively, and at the DDT and  $\gamma$ -BHC concentrations in water from 0.03 to 0.3  $\mu\text{g/l}$ .

Apart from investigations at the river watersheds, we studied the  $\gamma$ -BHC loss in runoff waters at the experimental runoff plot the snow cover of which was treated with  $\gamma$ -BHC before the snowmelt and at the similar untreated (background) plot (20 m x 5 m in size each). The coefficient of  $\gamma$ -BHC loss from the treated plot was 3.7% and from the untreated one - 0.2%. The depth of water runoff at these plots was approximately 2.5 times greater than that from the watersheds considered above.

Analysis of the DDT and  $\gamma$ -BHC loss coefficients obtained in spring showed that first, the loss coefficient value was directly proportional to the depth of water runoff, and second, the loss coefficient of just applied  $\gamma$ -BHC was an order higher than that of its residual amounts.

Special runoff plots were installed to investigate pesticide loss in runoff waters due to rainfall, 6 m<sup>2</sup> each. We determined the amounts of pesticides deposited with rain and lost in surface water



runoff due to a given rain as well as the pesticide content in soil. The maximum loss coefficient obtained at the 23.4 mm precipitation was  $2.5 \times 10^{-2}\%$  for  $\delta$ -BHC and  $3 \times 10^{-3}\%$  for DDT.

Thus, the results obtained show that the loss coefficients of organochlorine pesticides - DDT and  $\delta$ -BHC were low both at the natural watersheds and at the experimental runoff plots (tenth and hundredth fractions of percent). The  $\delta$ -BHC loss coefficient did not exceed 3.7% even when  $\delta$ -BHC was applied in the snow cover before the snowmelt, that is under the best runoff conditions.

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# HEXACHLOROCYCLOHEXANE, METAPHOS, AND CHLOROPHOS DECOMPOSITION IN SOIL AND THEIR MIGRATION WITH THE WATERS OF SURFACE RUNOFF

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Great quantities of chemicals and among them pesticides enter the biosphere due to intensive chemicalization of agriculture. Upon the influence of different factors the greater part of pesticides is decomposed in soil forming primary products and certain preparations are preserved in soil for a long time due to high persistency. Systematic usage of persistent pesticides and those with high cumulative properties at vast watersheds occupied by agricultural lands may result in pollution of natural waters.

In order to predict pollution of natural bodies by pesticides, it is necessary to study the rate of their decomposition in different soils, migration capability as well as to obtain quantitative characteristics of their removal from agricultural lands.

Studies of hexachlorocyclohexane (BHC), metaphos, and chlorophos decomposition in soil, their migration capability as well as the possibility of washing out by surface runoff were carried out at four runoff plots with the area 100 sq.m located in the zone of drought steppe.

The soil at the runoff plots was chestnut, semiloamy containing 3.8% of humus; pH was 7.45. The plots were treated with BHC and metaphos twice - in June, 1972 and 1973, while by chlorophos only in June, 1973.

In 1972 BHC was applied at the plots I and 2 at the rate of 120 g per each plot, while at the plots 3 and 4 metaphos was applied at the rate of 25 g per each plot. In 1973 the first plot was treated again by BHC at the same rate, the third plot was treated by metaphos twice - in June, 10 and 30 at the rate of 62.5 g. The fourth plot was also treated by chlorophos twice at the rate of 120 g and 300 g, respectively.

At the beginning of the experiment samples were taken every day with gradual increase of the interval between sampling up to 5 - 10 - 30 days. Soil samples were taken at 3-5 points from the depth of 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50 cm. Water samples were taken at the outlet of the runoff plots from I to 3 samples for the period of each rain flood.

Pesticides were determined by thin-layer chromatography.

Decomposition rate of pesticides in soil was not uniform and depended on meteorological conditions of the year. Dry 1972 was characterized by high temperature of air and soil surface in summer period. Average monthly temperature of air in June was 24°C, in July 26°C, maximum temperature was 40°C. Average temperature of soil at this period was 31°C, and maximum temperature was 65°C. Small precipitation (several rains in June with total sum of precipitation 47 mm, and in July 9 mm) resulted in the absence of runoff for this

period. Therefore in 1972 it was possible to study only the process of pesticide decomposition in soil.

1973 was more humid as compared to 1972. The temperature of air and soil surface was lower. Average monthly temperature of air in June was 19°C, in July - 21°C, maximum - 29°C. Average monthly temperature of soil was 24°C. Frequent and abundant rains (sum of precipitation in June was 109 mm, in July - 60 mm) were followed by short-term runoff from the plots.

In dry 1972 decomposition of BHC in soil proceeded slowly enough. In 10 days after treatment in the soil 80% of BHC were found, whereas in 20 days - 65%. The period of semidisappearance was 50 days. In about 1.5 years the BHC content decreased by 99%. Residues of the preparation (1 - 3 µg/100 g) were found in the soil in 2 years after the treatment (Fig. 1A, Table I).

Table I

Persistency of Pesticides in Soil

| Pesticides | Year | Period of semidis-<br>appearance, days | Period for 99%<br>disappearance, days |
|------------|------|----------------------------------------|---------------------------------------|
| BHC        | 1972 | 50                                     | 500                                   |
|            | 1973 | 2                                      | 40                                    |
| Metaphos   | 1972 | 3.5                                    | 17                                    |
|            | 1973 | 1.3-1.8                                | 8-13                                  |
| Chlorophos | 1972 | -                                      | -                                     |
|            | 1973 | 0.6-0.8                                | 8-10                                  |
| DDVP       | 1972 | -                                      | -                                     |
|            | 1973 | 1.4-1.5                                | 10-14                                 |

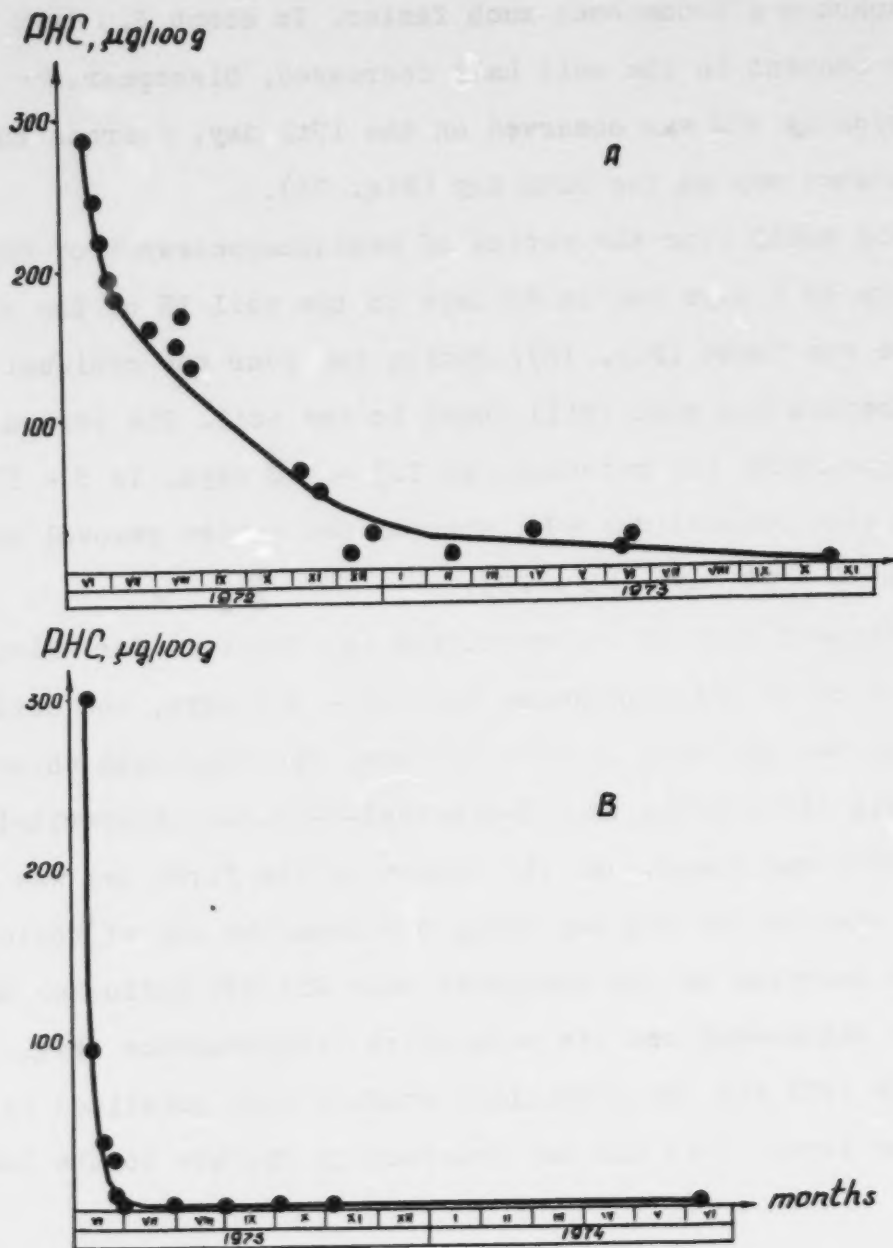


Fig. I - Change in nexachlorocyclohexane content in the upper 5 cm layer of soil.

A - Treatment in June, I<sub>7</sub>, I<sub>7</sub>/2

B - Treatment in June, I<sub>0</sub>, I<sub>973</sub>



Metaphos was decomposed much faster. In about 3.5 days the metaphos content in the soil half decreased. Disappearance of the preparation by 99% was observed on the 17th day, whereas the entire disappearance was on the 20th day (Fig. 2A).

In the humid year the period of semidisappearance of BHC decreased up to 2 days and in 40 days in the soil 1% of the applied substance was found (Fig. 1B). During the year the residual amounts of the preparation were still found in the soil. The period of semidisappearance for metaphos was 1.3 - 1.8 days. In 8 - 13 days the pesticide removal was 99%, whereas the entire removal was observed in 10 - 14 days (Fig. 2B).

The highest rate of decomposition was observed for chlorophos. The period of semidisappearance was 0.6 - 0.8 days, and entire disappearance was observed in 13 - 15 days. Together with chlorophos in the soil its metabolite O,O-dimethyl-O-(2,2-dichlorovinyl)-phosphate (DDVP) was found, and its amount on the first day was about 15 - 20%, that on the 5th day being 55% from the sum of toxicants. 2.5 times increase in the treatment rate did not influence the character of chlorophos and its metabolite disappearance (Fig. 3).

In dry 1972 all the pesticides studied were localized in the upper 5 cm layer. They did not practically migrate to the lower horizons.

Heavy rains in 1973 during the experiment stimulated pesticide transfer to the depth of the soil. Chlorophos and DDVP were the most mobile and their concentration in the 5-10 cm layer was 55 µg and 25 µg/100 g, respectively; in the 10-20 cm layer - 30 µg



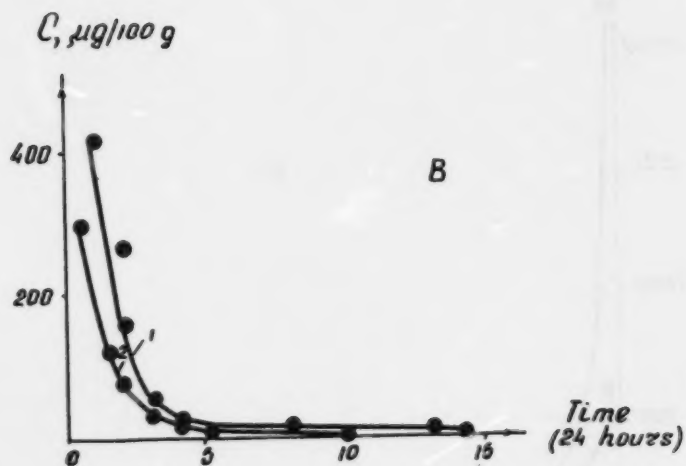
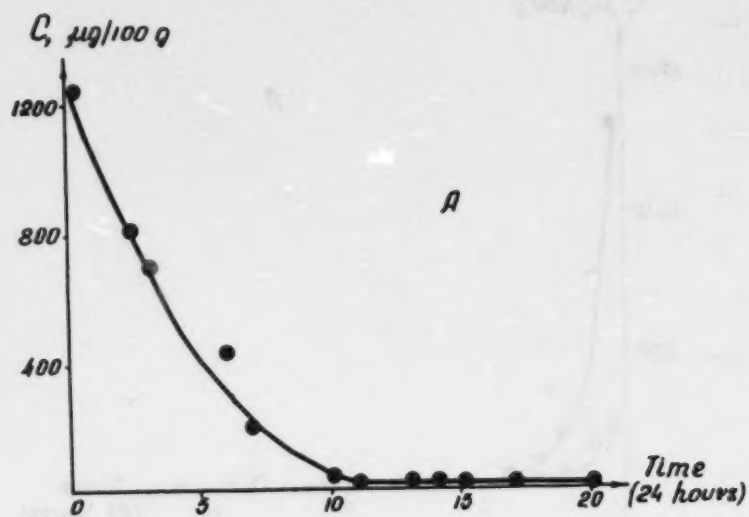


Fig. 2 - Change in metaphos content in the upper 5 cm layer of soil.

A - 1972

B - 1973 - 1 - Treatment in June, 10,

2 - Treatment in June, 30

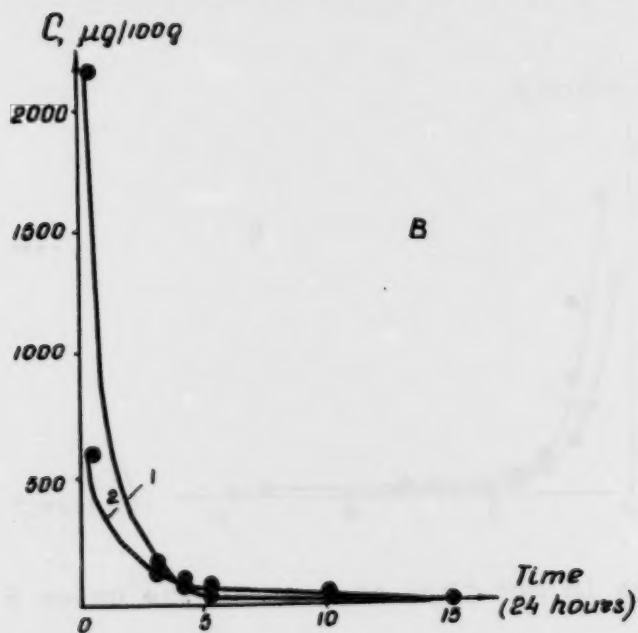
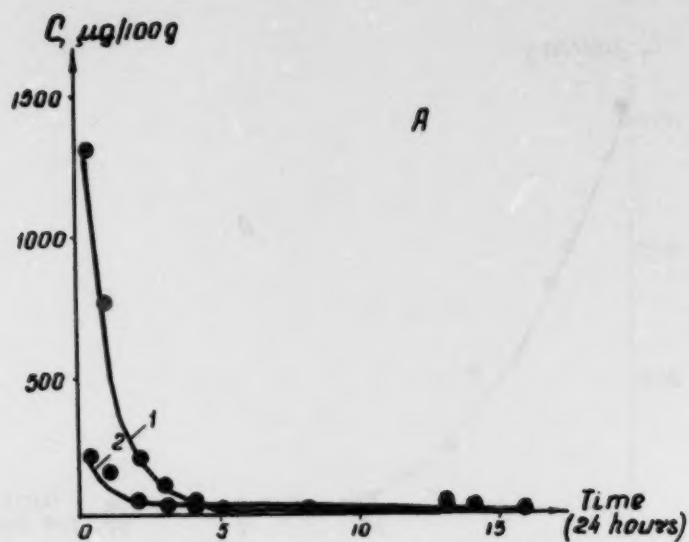


Fig. 3 - Change in chlorophos content and its metabolite DDVP (2) in the upper 5 cm layer of soil.

A - Treatment in June, 10, 1973

B - Treatment in June, 30, 1973.

and 16 µg/100 g, in the 20-30 cm layer - 16 µg and 12 µg/100 g. Metaphos content at the 5-30 cm depth varied from 1 to 5 µg/100 g. BHC migrated up to the depth of 60 cm. Pesticide concentration in the soil layer below 10 cm didn't exceed 18 µg/100 g of soil.

Mathematical processing of the obtained data according to the program of approximating equation <sup>choice,</sup> showed that decomposition of the investigated pesticides in the soil is given by the following equation:

$$C = \frac{at + b}{et + d} \dots\dots\dots (I)$$

where C - concentration of preparation;

t - time

a, b, e, d - coefficients.

Coefficient values for dry and humid year differ by many times.

For example, the equation for metaphos decomposition under the dry year is given by:

$$C = \frac{0.1554 + (-2.0109)}{(-0.0007) \cdot t + (-0.0021)} ;$$

for the humid year

$$C = \frac{0.0719 + (-0.9044)}{(-0.0022) \cdot t + (-0.0001)}$$

Study of pesticide removal by surface runoff from the experimental runoff plots showed that its value is proportioned directly to the quantity of applied pesticide and runoff volume and in-

directly to the period between treatment of the field and the beginning of the flow.

Pesticide removal didn't exceed 0.03% for BHC, 0.04% for metaphos, and 0.23% for chlorophos (together with DDVP) of the quantity applied (Table 2).

Table 2

Pesticide Removal with Surface Runoff

| Pesticide         | Pesticide Removal from 1 ha |            |
|-------------------|-----------------------------|------------|
|                   | g                           | %          |
| BHC               | 4.0                         | 0.03       |
| Metaphos          | 0.01-2.35                   | 0.001-0.04 |
| Chlorophos + DDVP | 0.2-67.5                    | 0.002-0.23 |

## PARTITIONING AND UPTAKE OF PESTICIDES IN BIOLOGICAL SYSTEMS

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Natural bodies of water, blood and plant sap were compared as aqueous flow systems for transporting pesticides and other chemicals. The uptake and distribution of pesticides in biological systems were related to water solubility; volatility from water; adsorption to soil organic matter, plant and animal organisms in aquatic ecosystems; effects of temperature; type of flow system; route of pesticide intake; specific types of organism tissue; and ratio of biomass to surface area for sorption. Differences between bioadsorption and bioabsorption were discussed. Partition coefficients between *n*-octanol and water; soil and water; and water and air are important guides to the bioaccumulation potential of pesticides.

Pesticides, just like other chemicals, are taken up and distributed in gas, liquid, and solid phases of the environment. They distribute by flow systems (mainly water or air) to surfaces to which they adsorb to and are often absorbed by living organisms and return changed or unchanged to flow systems inside or outside of organisms. Three important environmental aqueous flow systems are bodies of water, blood, and plant sap which, while variable in flow rate, have the ability to rapidly distribute solutes and particulates to adsorptive surfaces, organisms, organs, and/or cells. These three transport systems are composed percentage-wise mainly of water; however, they contain small amounts of many chemicals with similar functional groups in common which modify the dominance of water. Because of these distribution systems, partitioning of pesticides in and from flow systems can be expected to occur onto surfaces according to inherent physical and chemical properties of the pesticide such as volatility, water and fat solubility, and sorption to

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solids in the presence of flow systems. Plant and animal organisms contain and release water, food, and pesticides by partitioning them through surfaces, organs, and cell barriers.

Pesticide volatility from water appears to increase with increasing amounts of water evaporation, and decreasing water solubility. Thus, even DDT is relatively quite volatile from water; however, this may be influenced by cosolvents (such as soil organics) or competitive adsorptive surfaces of soils in water such as soil particulates or plants or animals.

Sorption of most pesticides, while variable on the mineral portion of soil, is mainly correlated with the soil organic matter content which has ingredients having sorptive capacity for both ionized and unionized, and fat and water-soluble pesticides. The effect of the pH of soil on sorption of acidic and basic compounds may also be important. Sorption on soil and organisms takes place most rapidly under the greatest concentration differential between the flow system and sorptive surface. Typically well over 50% of the total adsorptive uptake of pesticides occurs in the first few hours of exposure. While the total amount of pesticide adsorbed on carbon and algae increases with increasing concentration in the flow system (water), the concentration factor may decrease with increasing pesticide concentration in water. Clearance of pesticides from tissues is not necessarily at the same rate as uptake, and is often slower. Other factors affecting adsorption are temperature, speed of circulation of the flow system, ratio of biomass to flow system volume, and mode of intake of pesticide into the organism.

The distribution of DDT and other stable chemicals in fat of animal organisms, if given sufficient time for equilibration, appears to roughly correlate with the n-octanol:water partition coefficient obtained as a guide to the bioconcentration factor in fat tissues of animals from aqueous sources. This factor alone can be somewhat difficult to correlate with fat under some conditions since, in fish, fat is variously distributed in tissues at different ages, stages of sexual development, and seasons of the year, sometimes being rather uniformly distributed and other times not. Also some fat tissues appear to be more rapidly metabolized than others and, therefore, release pesticides into the blood at various times of stress or according to the need for the fat. The greater the number and volume of components in an ecosystem, the greater the complexity of the distribution of the available pesticide from water, and less likely the expectation of extremes in bioaccumulation. The distribution of a water and organic soluble compound like dalapon as indicated by the n-octanol:water partition coefficient, is in great contrast to DDT, since it does not volatilize at a rate significantly different from water, nor partition in favor of animal organisms, or their fat, but does accumulate in some plant organisms. Herbicides like 2,4-D and 2,4,5-T

partition somewhat similarly to dalapon, but when made into an oil soluble (the butyl ester) form, the octanol:water partition coefficient is considerably higher. However, this is not very significant in nature since the ester bond is not very stable in animal organisms, and thus the ester does not continue to bioaccumulate like DDT. Every chemical has a uniqueness in its combination of physical and chemical properties, and in the way in which it will act in the environment.

From pesticide bioaccumulation data it is apparent that the first period of residue pickup is due to adsorption and is often related to high surface area to mass ratio of the adsorbent and may result in high residues. With many pesticides no further significant uptake of residue after the first day is made during a continued exposure period of days or weeks. However, if the pesticide is high in fat solubility, low in water solubility and persistent in the environment, a continued increase in residues may take place over time until a steady state (equilibrium) point is reached in live organisms. Such residue pickup is by absorption and such bioaccumulating chemicals can be detected at an early stage by obtaining early baseline residue levels for comparison with later levels. Other very useful partition coefficients to obtain in addition to n-octanol to water are soil organic matter to water, and water to air. These partition coefficients can be calculated roughly from predetermined constants of water and n-octanol solubility and vapor pressure. These calculated coefficients are useful in determining potential of pesticides for leaching through soil, and uptake and distribution throughout the biota. Distribution coefficients of soil organic matter to water, and of aquatic animal organisms to water, are often of the same order of magnitude.

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## PESTICIDE TRANSPORT AND TRANSFORMATION IN PLANTS

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Pesticide use for crop protection in the United States has increased dramatically over the last 20 years. Sales at the user level (\$MM) in 1975 were estimated at 1,780 with a projected increase to 2,955 by 1980. The most impressive gains have been in the use of herbicides (65%), followed by insecticides (25%) and fungicides (6%). In the past ten years, increased registration requirements and environmental safety concerns have prompted rapid developments in research on the behavior and fate of these chemicals in higher plants. Major pathways of absorption, movement, and metabolism have been established for many herbicides and insecticides and a limited number of fungicides.

Metabolism studies have shown that pesticides undergo similar biotransformations in both plants and animals. Principal reactions include: oxidation, reduction, hydrolysis, and/or conjugation. Conjugation reactions are of particular importance in plants because, in contrast to animals, conjugated plant metabolites are not excreted. Instead, they may be stored or incorporated into insoluble "terminal" residues and ultimately degraded in the environment or ingested by animals, including man.

Pathways of metabolism are affected by pesticide application methods and different routes of absorption by the plant. In the soil, pesticides may be transformed by microorganisms prior to root uptake while foliar applications may result in photolytic and/or hydrolytic action prior to absorption by fruit or foliage. Tissue differences in metabolism also may be a factor in the disposition of pesticide metabolites. Other factors that may affect the behavior and fate of pesticides in plants include: interactions with other pesticides or chemicals, growth and development, environmental stress, nutrition, disease and genetic variations.

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Selected examples of herbicide and insecticide metabolism studies are presented to illustrate the advantages, disadvantages, and limitations of current research approaches to investigations of pesticide uptake and transformation in higher plants.

#### INSECTICIDE STUDIES

Recent plant metabolism studies (22, 24, 25) have focused on three thioaryl organophosphorous insecticides: fonofos (O-ethyl S-phenylethylphosphonodithioate), N-2596 (O-ethyl S-4-chlorophenyl ethylphosphonodithioate), and carbophenothion S-[(p-chlorophenylthio)methyl]O,O-diethylphosphorodithioate. The metabolic fate of these compounds in animals was reviewed recently (26).

The fate of fonofos was studied in Irish potatoes as a representative root crop. In separate but identical experiments, sprouting potato pieces were planted in soil containing 2.64 ppm ( $\alpha$ -ethoxy- $^{14}\text{C}$ ) or (phenyl- $^{14}\text{C}$ )-fonofos. Plant material, including foliage, tuber peel, and pulp was analyzed through 87 days after planting (22).

The proposed metabolic pathway of fonofos in the potato plant is shown in Figure 1. Metabolites were isolated and identified by thin-layer chromatography, radio-gas liquid chromatography, hydrolysis, enzymatic cleavage, derivatization and mass spectrometry. Fonofos is metabolized extensively to phosphonic acid derivatives; O-ethylethane-phosphonic acid (EOP) and O-ethylethanephosphonothioic acid (ETP). Only trace amount of the O-ethyl S-phenylethylphosphonothiolate (oxon) were recovered suggesting that this metabolite may be a reactive intermediate and degrades rapidly to EOP and thiophenol (PSH). The leaving thiophenyl moiety of fonofos and/or its oxon is metabolized via S-methylation and sulfoxidation to methyl phenyl sulfide (PhSMe), methyl phenyl sulfoxide (PhSOMe), methyl phenyl sulfone (PhSO<sub>2</sub>Me) and unidentified polar products, possibly conjugates. Based on the overall similarity of the metabolic pathway of fonofos in animals (23) and the plant, it is suggested that the polar plant products contain the PhSO<sub>2</sub>Me moiety. The S-methylation reaction provides an efficient means for thiophenol detoxification and has not been reported previously in plants.

Metabolism studies with (phenyl- $^{14}\text{C}$ ) N-2596 in corn plants are summarized in Figure 2. Plants were grown to maturity in soil treated at the rate of 6.0 ppm N-2596. In addition to S-methylation and sulfoxidation, the cleaved 4-chlorothiophenyl moiety was oxidized to 4-chlorophenyl sulfonic acid (4-ClPhSO<sub>3</sub>H) by another pathway. The sulfonic acid was the major "terminal" metabolite of N-2596 in the plant and accounted for 48.7% of the recovered radiocarbon. This metabolite was also identified in rat urine (27). Again, the O-ethyl S-4-chlorophenylethanephosphonothiolate (oxon) appears as a very minor metabolite in the plant, but may serve as a reactive intermediate in the formation of 4-chlorothiophenol (4-ClPSH) and subsequent metabolic products. However, the same metabolic products could also arise directly from cleavage of N-2596. It is noteworthy that apparently no thioaryl hydroxylation products were detected in plants either as free phenols or as conjugates. Of the total radiocarbon recovered in plant tissues, 75% (4763 ppb) was identified, 11% (697 ppb) were unknown products and 15% (970 ppb) was "bound"



or unextractable radiocarbon. The total radiocarbon in mature corn plants was calculated as 6.43 ppm equivalents of N-2596.

Carbophenothion, with a thio-ether moiety, presents a more complex metabolic pathway in animals (3, 26) and plants (2, 25). Under field conditions, following application to lettuce (2), carbophenothion was oxidized to its sulfoxide (II) and sulfone (III) and to the thiophosphate (IV) and its sulfone (VI) (Figure 3). Trace levels of these oxidation products were present up to 14 days after treatment. When (phenyl- $^{14}\text{C}$ ) carbophenothion was applied as an emulsion to foliage and maturing fruit of a greenhouse-grown orange tree, much of the dose was lost through volatilization and, to a lesser extent, by metabolic transformations (24). Thin-layer chromatographic and co-chromatographic analyses of plant tissue extracts with reference standards established the presence of carbophenothion and all five oxidation products (II, III, IV, V, and VI), in the foliage and the orange peel but not in the juice and pulp. Of the applied radiocarbon, polar unknowns accounted for 7.1% in foliage, 13.1% in peel, and 0.5% in juice and pulp. These studies also established that essentially no radiocarbon was translocated to untreated fruit and foliage.

As indicated in the introduction, these three studies are indicative of some of the difficulties encountered in the isolation and identification of polar plant metabolites and "bound" residues. Furthermore, as indicated in the case of carbophenothion, it is difficult to separate photolytically induced biotransformation products from those formed by action of the plant itself.

#### HERBICIDE STUDIES

Metabolism studies with monuron {3-(4-chlorophenyl)-1,1-dimethylurea}, other substituted 3-(phenyl)-1,1-dimethylurea herbicides, and their metabolites have established the major pathways of urea herbicide metabolism in cotton and other plant species (7, 8, 10) (Figure 4). An initial sequential oxidation of N-methyl groups is catalyzed by a microsomal mixed function oxidase (5, 7, 28, 36). Unstable N-hydroxymethyl intermediates are either conjugated as O-glucosides or degraded rapidly to less toxic demethylated products and formaldehyde (5, 7, 8, 37). Hydrolytic formation of substituted anilines is negligible. A second oxidative pathway of urea herbicide metabolism has been reported recently (10, 20, 21). Monuron and its demethylated metabolites, 3-(4-chlorophenyl)-1-methylurea and p-chlorophenylurea, may also be aryl hydroxylated and conjugated as phenolic glucosides.

Comparative metabolism studies with tomato, pepper, cotton, okra, peanut, soybean and tobacco plants show that diphenamid (N,N-dimethyl-2,2-diphenylacetamide) is metabolized primarily via a sequential oxidative N-demethylation pathway similar to the substituted 3-(phenyl)-1,1-dimethylurea herbicides (14, 15, 16, 17) (Figure 5). Aryl hydroxylation is a minor pathway in most of the plant species studied and hydrolysis of the amide bond is negligible. Two major glycoside conjugates have been isolated from diphenamid-treated tomato plants and identified as the glucoside and the gentiobioside of the initial oxidative N-demethylation intermediate, N-hydroxymethyl-N-methyl-2,2-di-

phenylacetamide (13). Low level ozone fumigation (10-34 pphm) of diphenamid-treated tomato and pepper plants stimulates glycoside formation, but has little effect on root absorption, translocation, or pathways of metabolism (13, 14, 15, 16).

Three metabolic and detoxication pathways have been established for substituted 2-chloro-s-triazine herbicides in higher plants (31) (Figure 6). The principal pathway in tolerant plants involves a rapid initial conjugation with glutathione (18). The enzyme responsible for glutathione conjugation, a glutathione S-transferase, has been isolated and partially characterized from corn (6, 7). It is a major factor in the tolerance and selectivity of 2-chloro-s-triazines in corn, sorghum and sugarcane (18, 29, 30, 32). Recent studies (19) show that initial glutathione conjugate formation is followed by a series of additional biotransformations in sorghum. The heterocyclic s-triazine ring structure remains intact and appears to be incorporated into insoluble plant residues (31). Feeding studies with rats and sheep show that insoluble plant residue fractions are rapidly excreted in the feces and not incorporated into body tissues (1).

In studies with excised pea and peanut tissues and with peanut cell suspension cultures, the initial metabolic reaction of flurodifen (2,4'-dinitro-4-trifluoromethyl-diphenylether), is a glutathione S-transferase catalyzed cleavage of the diphenylether bond (9, 33) (Figure 7). Cleavage products of the reaction are S-(2-nitro-4-trifluoromethylphenyl)-glutathione and p-nitrophenol. The phenolic cleavage product is rapidly conjugated with glucose to yield p-nitrophenyl- $\beta$ -D-glucoside. Subsequent metabolism of the glucoside results in the formation of p-nitrophenyl-6-O-malonyl- $\beta$ -D-glucoside (34). Further metabolism of the glutathione conjugated cleavage product also occurs and recent studies (35) have identified S-(2-nitro-4-trifluoromethylphenyl)-N-malonyl-cysteine as a major flurodifen metabolite in peanut.

Cisanilide (cis-2,5-dimethyl-1-pyrrolidinecarboxanilide) metabolism studies with excised leaves and cell suspension cultures of carrot and cotton have been compared (11). Initial oxidation products, 2,5-dimethyl-1-pyrrolidine-4'-hydroxycarboxanilide and 2,5-dimethyl-3-hydroxy-1-pyrrolidinecarboxanilide, are conjugated as O-glucosides (Figure 8). Little, if any, hydrolysis of the herbicide molecule occurs. Recent studies indicate that the initial phenol oxidation product of cisanilide metabolism (2,5-dimethyl-1-pyrrolidine-4'-hydroxycarboxanilide) is the precursor of a "bound" residue fraction associated with the cell wall (12). Animal feeding and soil degradation studies indicate that the bioavailability of this "bound" residue fraction is limited.

#### CONCLUSION

Future research on pesticide transport and transformation in plants should include: the development of better methods and new techniques for the isolation, identification, and analysis of metabolites, degradation products, and terminal residues; increased studies on pesticide interactions; additional studies to determine the significance of environmental stress and genetic variation of factors affecting pesticide behavior, persistence and fate; and

expanded efforts to isolate and characterize key enzymes responsible for pesticide metabolism and detoxication.

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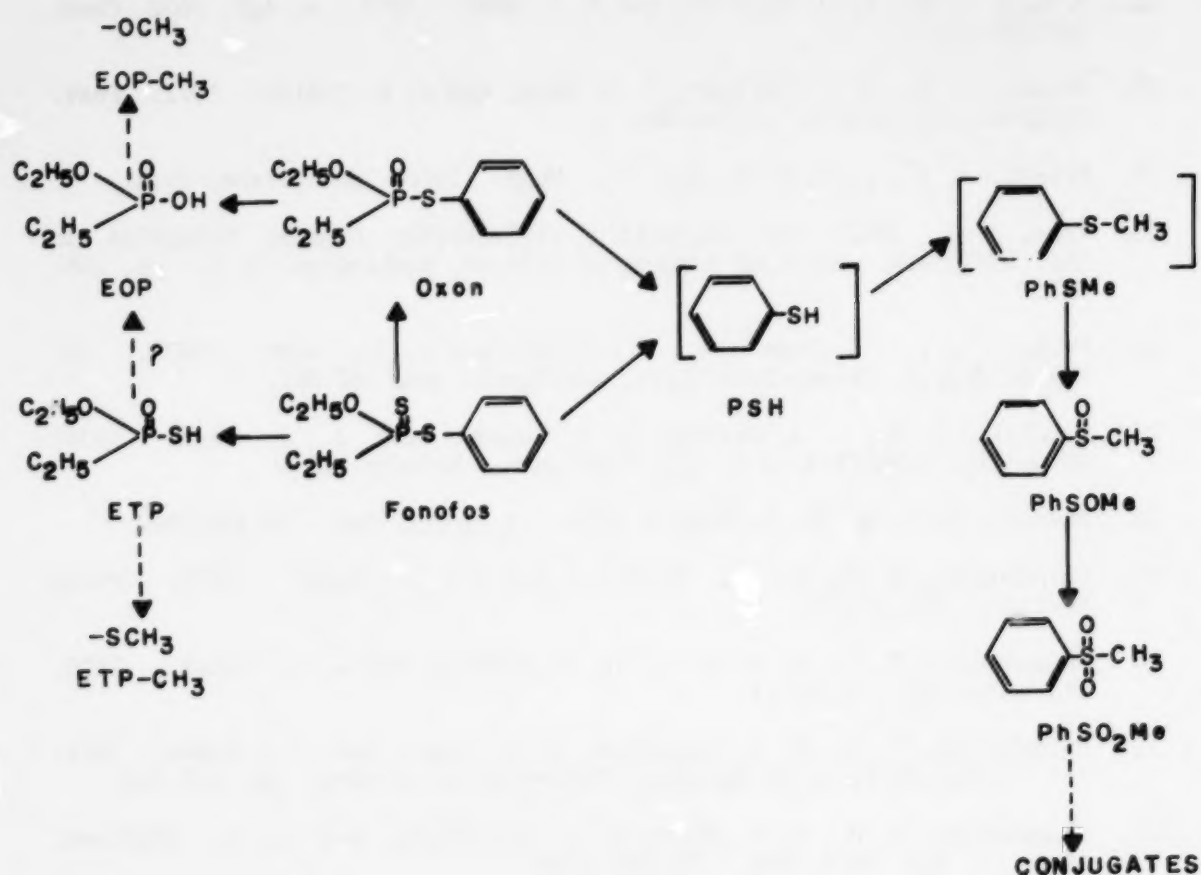


Figure 1. Proposed metabolic pathway of fonofos in potato plant (22).

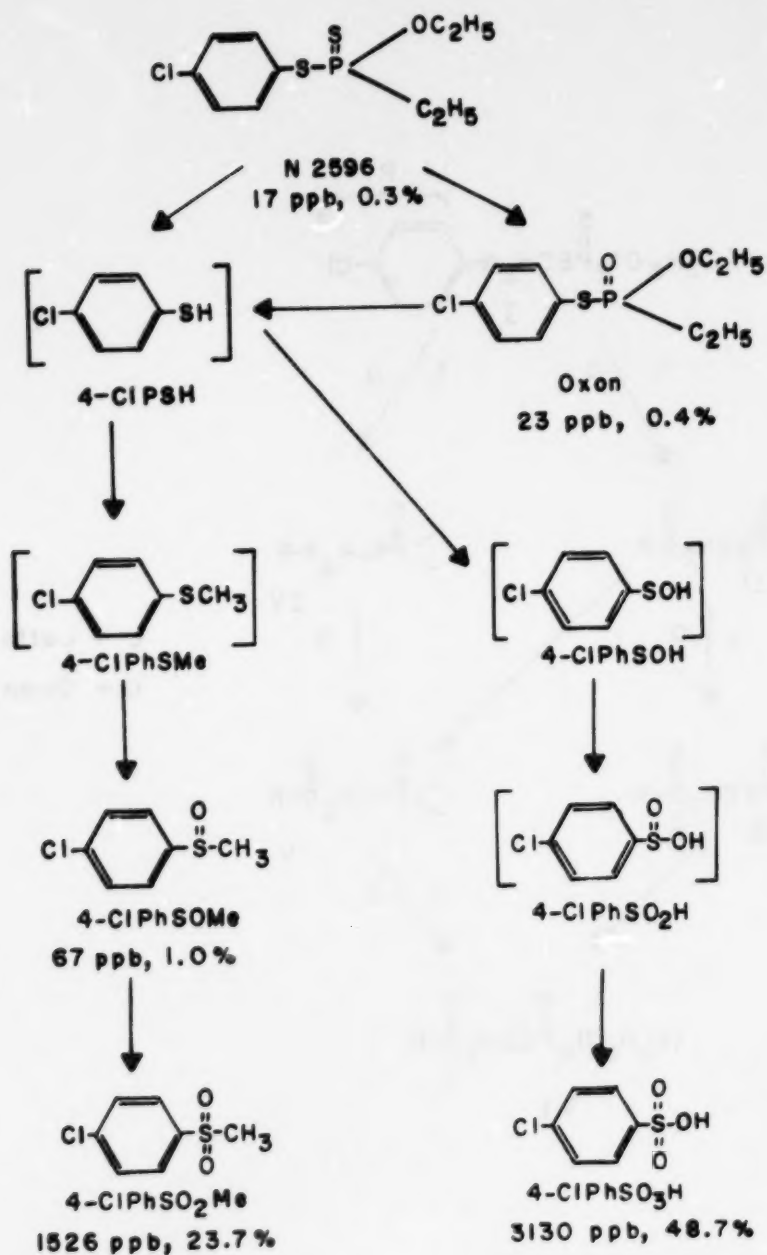


Figure 2. Proposed metabolic pathway of N-2596 in mature corn plants.

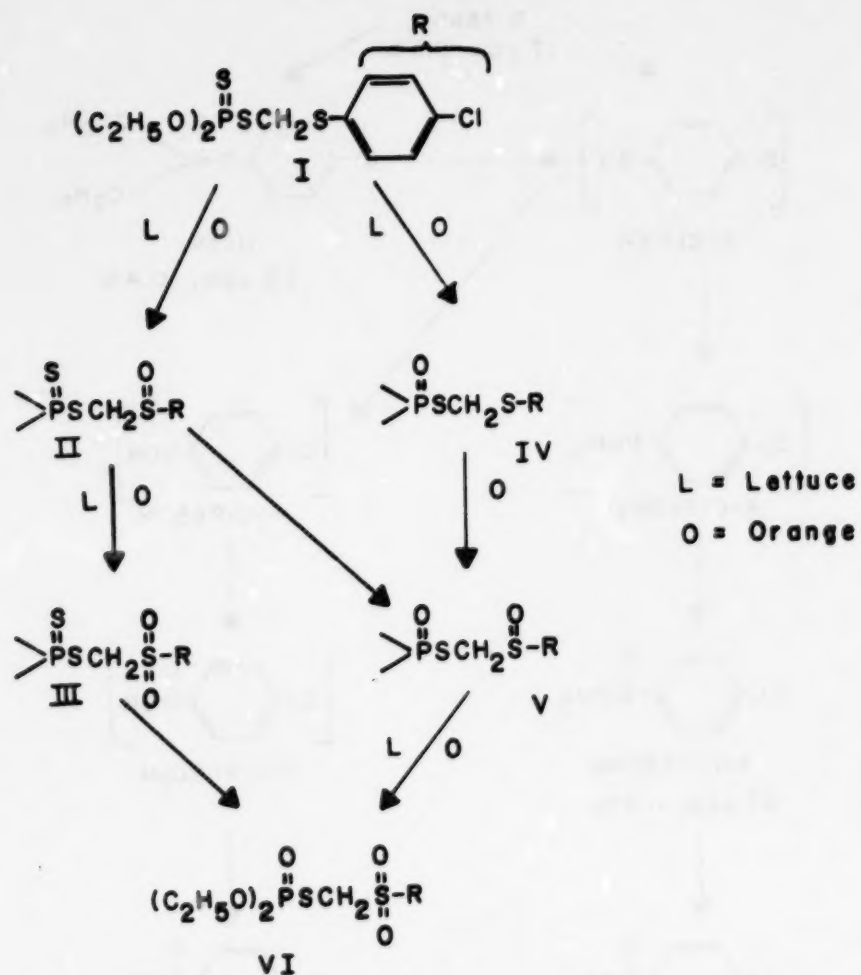


Figure 3. Oxidative metabolism of carbophenothion in lettuce and orange.

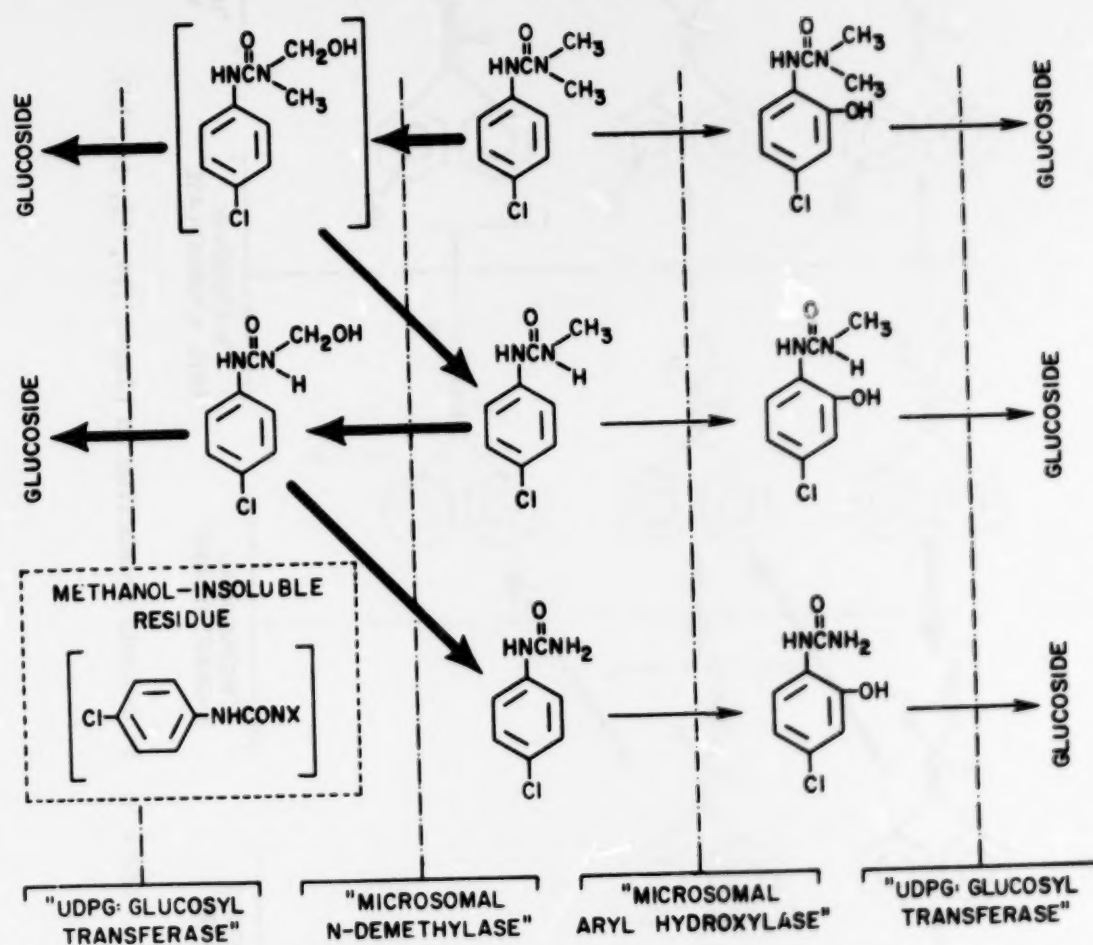


Figure 4. Monuron metabolism in plants (8, 10, 20, 21).





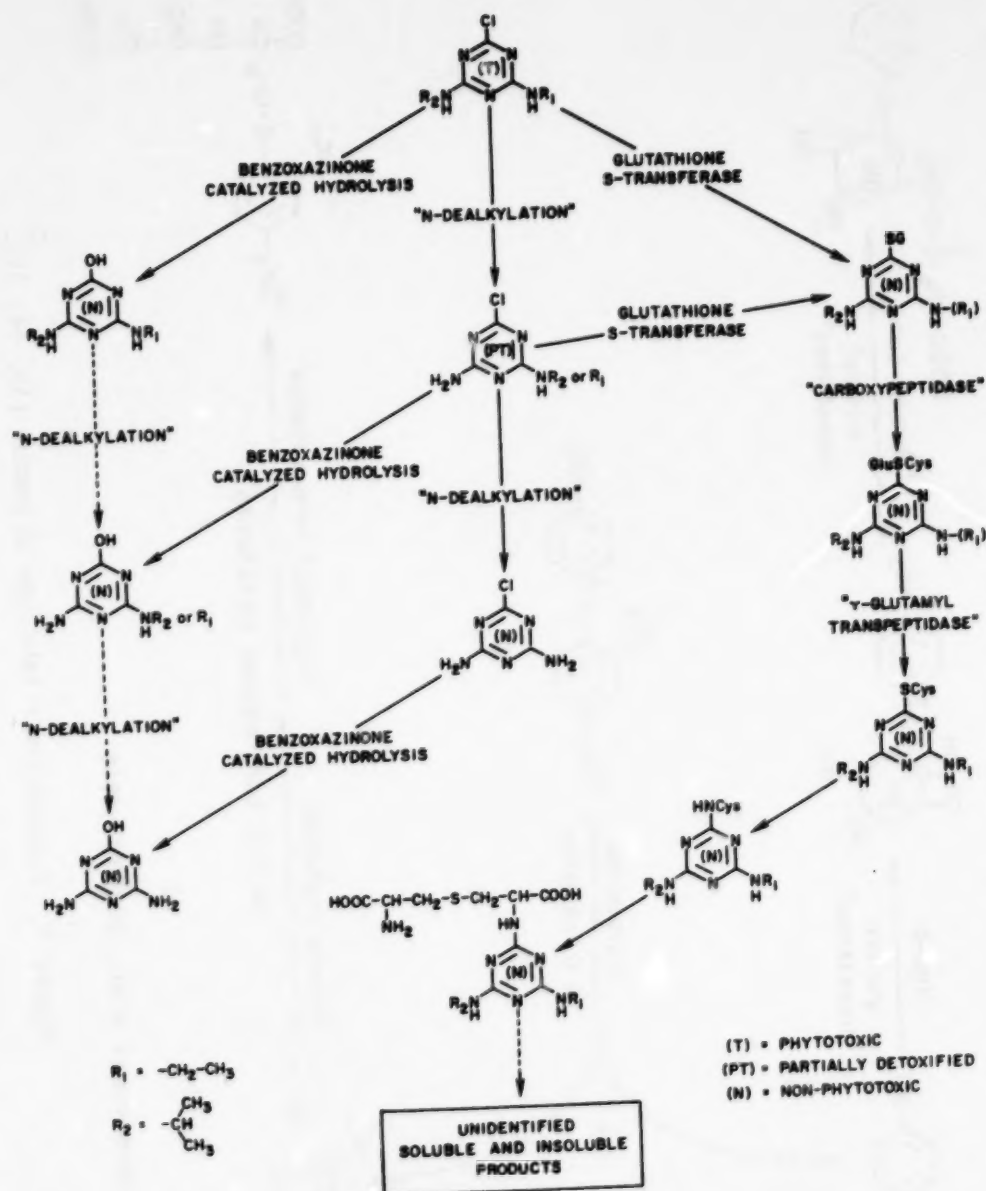
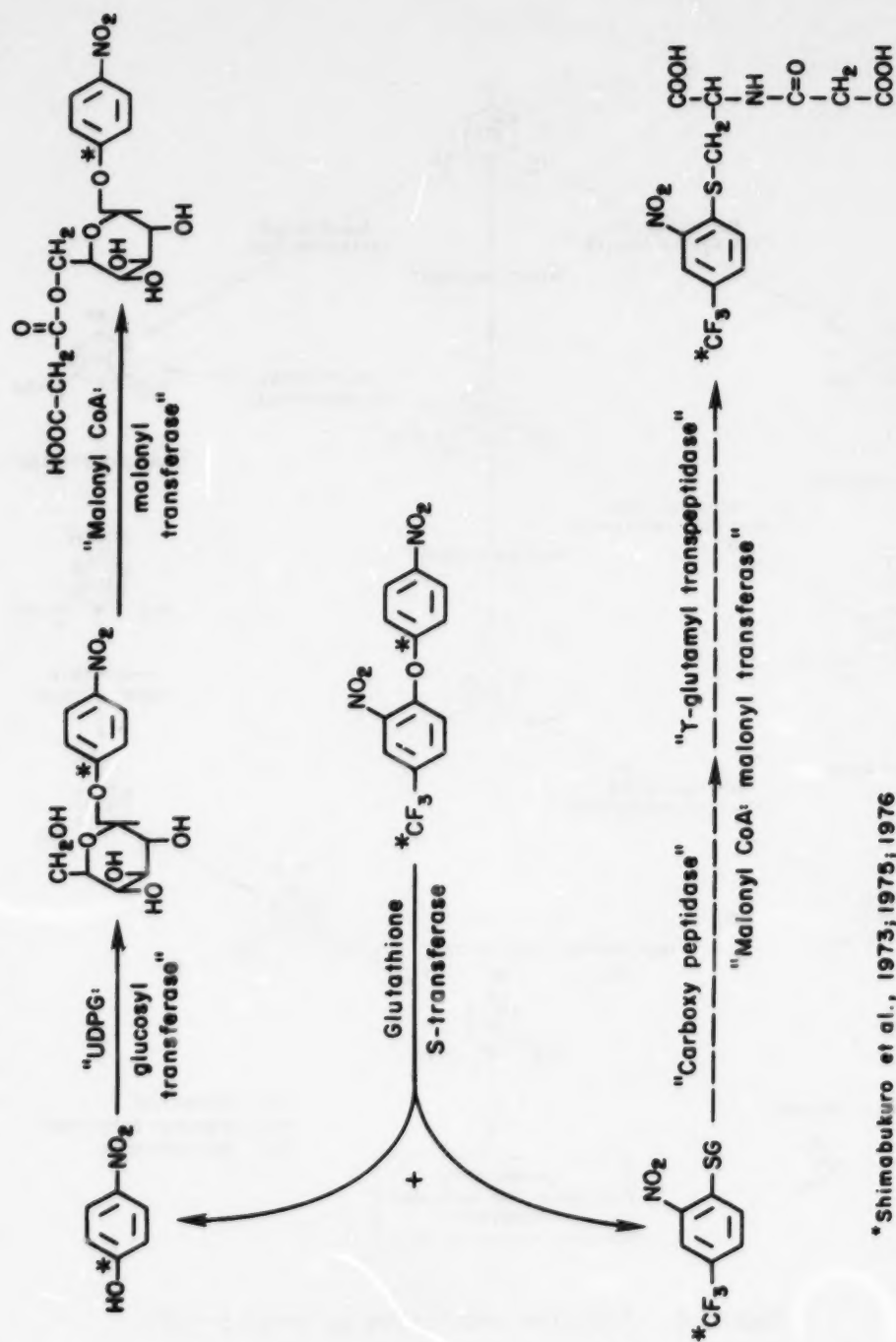


Figure 6. Atrazine metabolism in sorghum (19).



\*Shimabukuro et al., 1973; 1975, 1976

Figure 7. Fluorodifen metabolism in peanut (33, 34, 35).

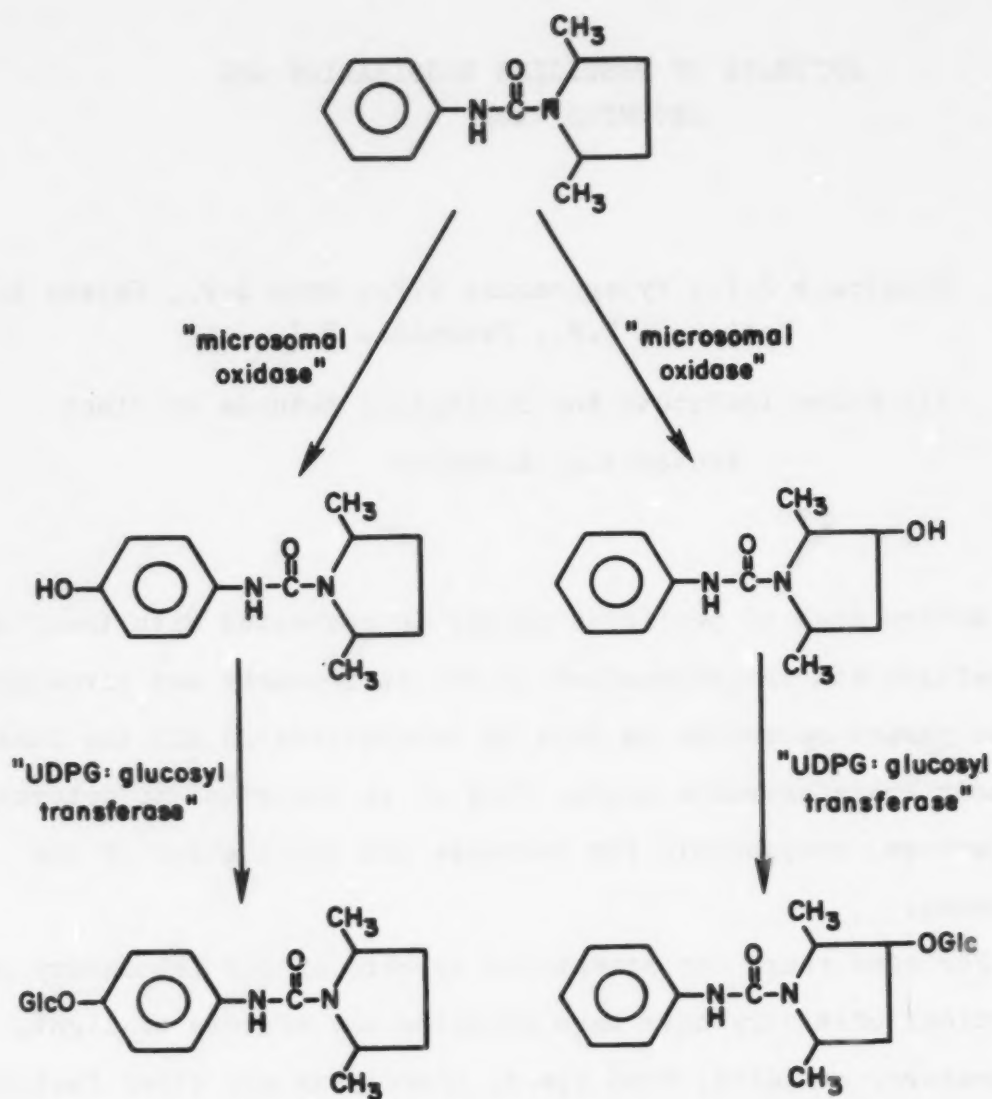


Figure 8. Cisanilide metabolism in plants (11, 12).



## PATHWAYS OF PESTICIDE DISSIPATION AND DECOMPOSITION

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Modern idea of pesticide danger is connected with their decomposition and transformation in the environment and circulation of the parent compounds as well as metabolites in all the links of their transformation cycle. Thus it is important to determine the factors, responsible for decrease and dissipation of the compounds.

For some years the scientific workers of our laboratory on analytical chemistry have been studying the effects of light, temperature, humidity, wind speed, hydrolysis and other factors on the stability of gardona, methylnitrophos, cianox, phosalone, phthalophos( imidane) and s-triazines on/in plant, soil by means of thin-layer-, gas chromatography and other methods of analysis.

In model studies under laboratory and field conditions the sunlight and air temperature at which the interaction with

the plant occurs, were proved to be the main factors, that contribute to gardona decrease and conversion on the treated apple tree.

Gardona, exposed to the sunlight, decomposes into a number of products, the main of them being cis-isomer of gardona. The organochlorine metabolites (2,4,5-trichloroacetophenone, 2,4,5-trichlorophenoacylchloride and oth.) were detected in significantly lower amounts. The kinetics of gardona photodecomposition and formation of the photolysis products under UV- and sunlight influence have been studied. The kinetic photodecomposition curves (Fig.1) of chemically pure and technical gardona under sunlight influence show that the technical product decomposes more quickly.

In the studies on the dynamics of gardona decrease on apple leaves and fruits (Fig.2) protected and non-protected against sunlight, the latter was shown to be an essential factor in the process of gardona decomposition.

In the interaction of gardona with the plant other metabolites are also formed, of which 2,4,5-trichlorophenyl ethanol in free and bound state is the most interesting one. In this case decomposition rate of gardona depends on air temperature. Other factors of the environment (wind, rain falls) influence insignificantly gardona decrease off the plant.

While studying the evaporation rates of methylnitrophos-  
O,O-dimethyl-O-(3-methyl-4-nitrophenyl)-thio-phosphate and cia-

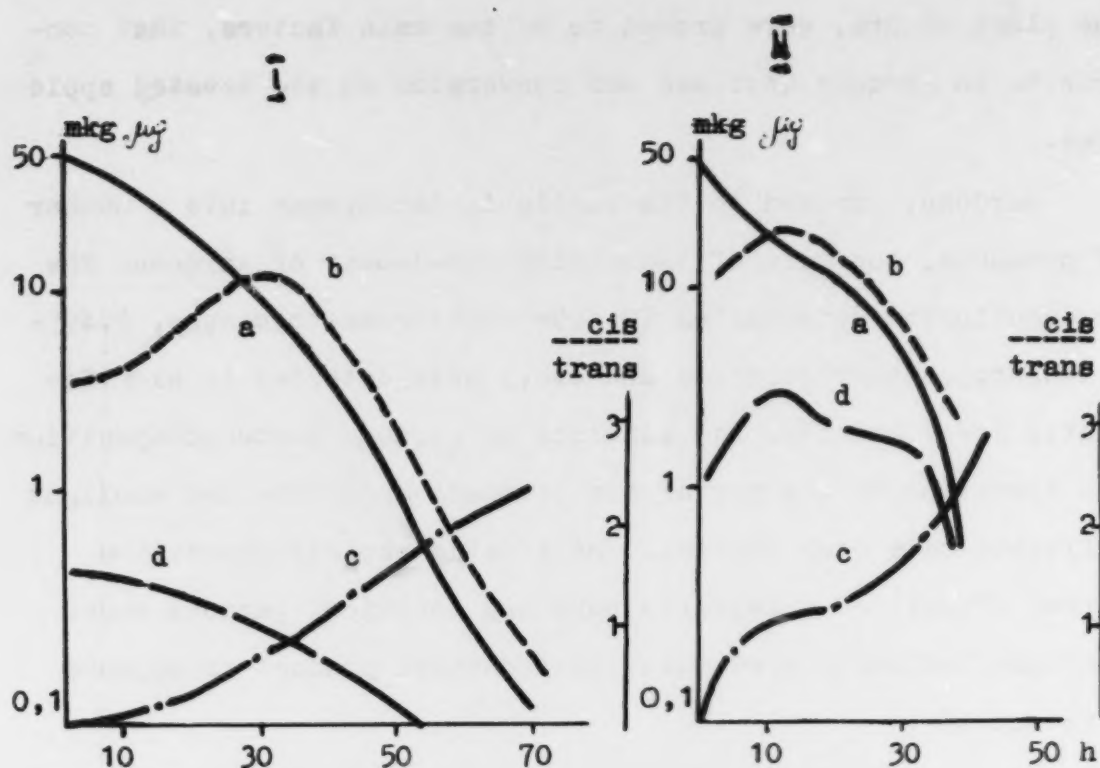


Fig. I. The kinetic curves of the photoalteration of Gardona by sunlight.

The irradiation: I - of the thin film of chemical pure Gardona; II - of the thin-film of wettable powder.

The kinetics curves: a - Gardona, b- cis-isomer of Gardona, c - the ratio cis/trans, d - 2,4,5 -trichlorophenacyl chloride.

nox-0,0-dimethyl-0-(p-cyanophenyl)-thiophosphate under controlled laboratory and field conditions, the compounds were shown to disappear quickly from the glass surface. Supposing that the process of insecticide loss is similar to the process of radio-

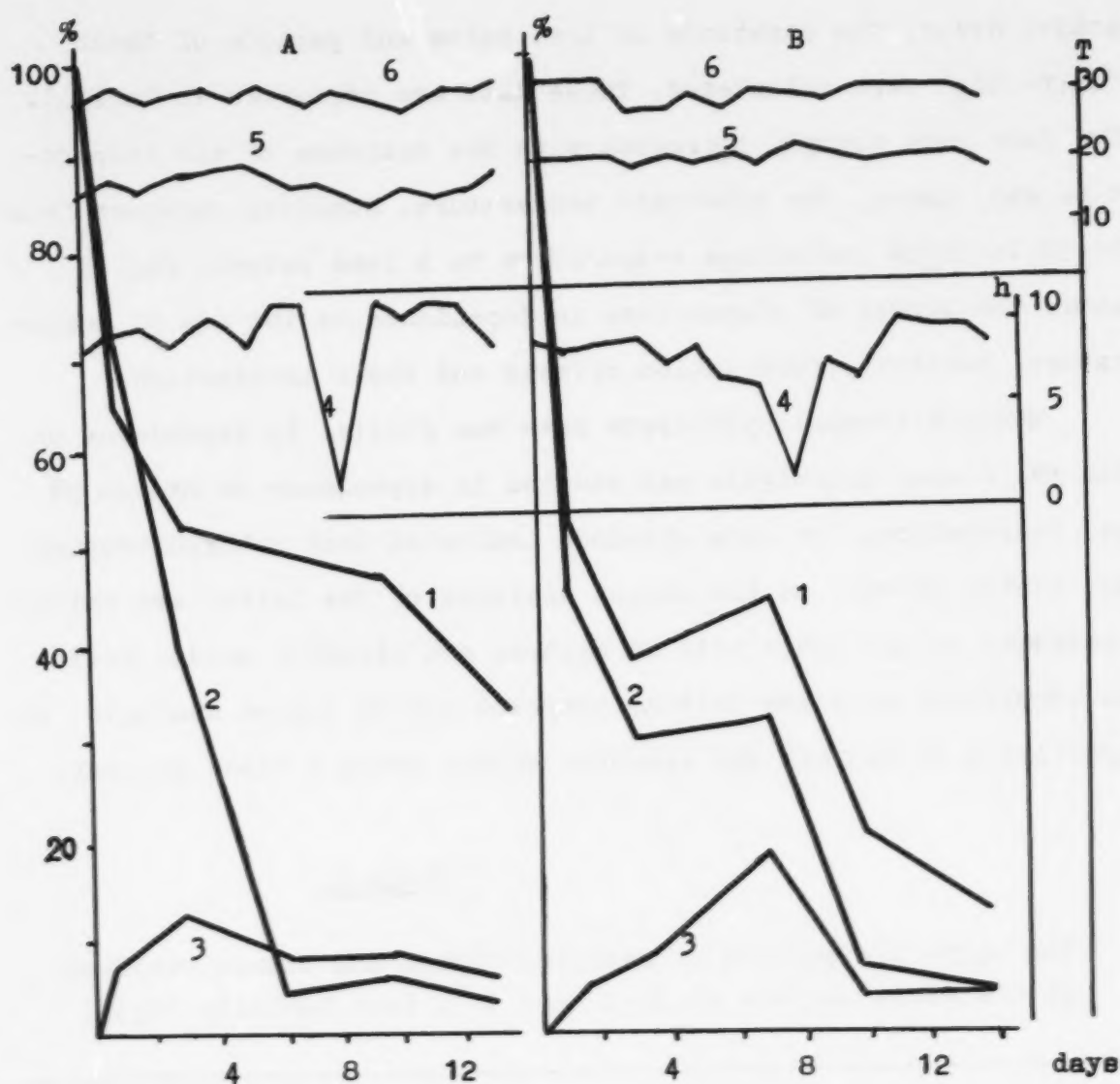


Fig.2. The dynamics of Gardona breakdown on leaves (A) and apples (B).

- 1 - protected from sunlight
- 2 - exposed to direct sunlight
- 3 - dynamics of cis-isomer Gardona
- 4 - the duration of day light, hours
- 5 - min. temperature of air,
- 6 - max. temperature of air.

active decay, the constants of loss rates and periods of their "half-life" were calculated. These data are presented in Table I. The loss rate sharply increases with the increase of air temperature and, hence, the substrate temperature. Humidity increase from 55±5% to 90±5% influences evaporation to a less extent. Fig. 3 shows the curves of cianox loss in dependence on the sum of temperature, humidity, formulation effects and their interaction.

Methylnitrophos hydrolysis rate was studied in dependence on the pH. Cianox hydrolysis was studied in dependence on medium pH and temperature. The data obtained indicated that methylnitrophos and cianox as well as the oxygen analogue of the latter are rather resistant to the hydrolysis in neutral and slightly acidic media. In comparison with the initial compound cianox oxygen analogue is hydrolyzed in neutral and slightly acidic media 2 times quicker.

Table I.

The half-life periods of methylnitrophos and cianox residues on the glass surface at 20-22 and 40°C (air humidity 55±5%)

| Compounds             | :Methylnitro-<br>phos, c.e. | : Cianox,<br>c.e. | : :<br>Cianox,<br>w.p. |
|-----------------------|-----------------------------|-------------------|------------------------|
| The half-life :20-22° | 17,0                        | 29,1              | 21,1                   |
| 40°                   | 9,3                         | 2,8               | 2,1                    |

c.e. - concentrate emulsion

w.p. - wettable powder



Thus, methylnitrophos and cianox are characterized by comparatively high volatility but are rather resistant to the hydrolysis. Being low polar insecticides they are mainly evaporated from the treated surface. This is confirmed by our data on methylnitrophos and

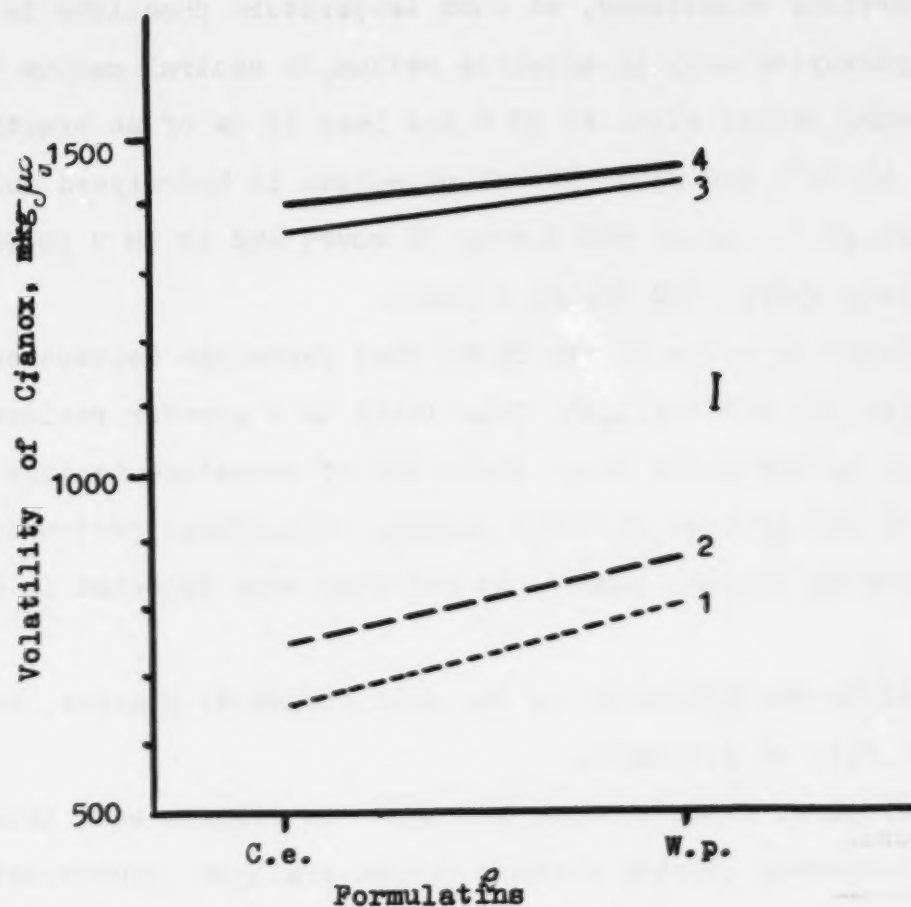


Fig.3 The dependence of the volatility of cianox from the main effects of: 1 - formulation, 2 - humidity, 3 - temperature, 4 - interaction of the factors.

The vertical line is L.S.D.<sub>05</sub> = 41.5  $\mu\text{g}$

cianox residue dynamics on apple fruits following treatment. As far as the evaporation process depends on temperature to a great extent, methylnitrophos and cianox are evaporated from treated apples at hot weather ( $28-33^{\circ}\text{C}$ ) for 1-3 days following spraying.

Phosalone is characterized by its relative hydrolytic resistance. Under laboratory conditions, at room temperature phosalone is quickly hydrolyzed only in alkaline medium, in neutral medium this process being rather slow. At pH 6 and less it is of no practical value. At  $60-70^{\circ}\text{C}$  and pH 5 50% of phosalone is hydrolyzed during 90 hours, at pH 7 - about 80% during 70 hours and at pH 9 phosalone is completely hydrolyzed during 4 hours.

In laboratory tests it was shown that phosalone decomposes slowly under UV- and sunlight. This leads to a greater residue persistence in harvested crop. About 50% of phosalone residue decomposes in the process of apple canning (blanching, pasteurization while preparing juices, puree). No residues were detected in apple juice.

Phosalone was preserved in the soil for about 2 weeks, when applied at rate of 3,0 kg/he.

Phthalophos, exposed to the sunlight on silicic acid thin layer plates, decomposes quickly forming oxygen analogue, hydroxymethylphthalimide, phthalimide and one unidentified compound, containing phosphorus ( $R_f=0,0$ ). The latter is formed in the greatest quantities. The parent compound is detected during 10 days and the oxygen analogue - during 25 days. Under irradiation of phthalophos in film (after solvent evaporation) oxygen analogue traces and the same unidenti-

fied compound are formed. The phthalophos decomposition under luminiscent lamp irradiation (450-700 nm) is identical to the decomposition under sunlight. The period of phthalophos semidecomposition was 95 hours. UV light accelerates photolysis processes (Fig.4).

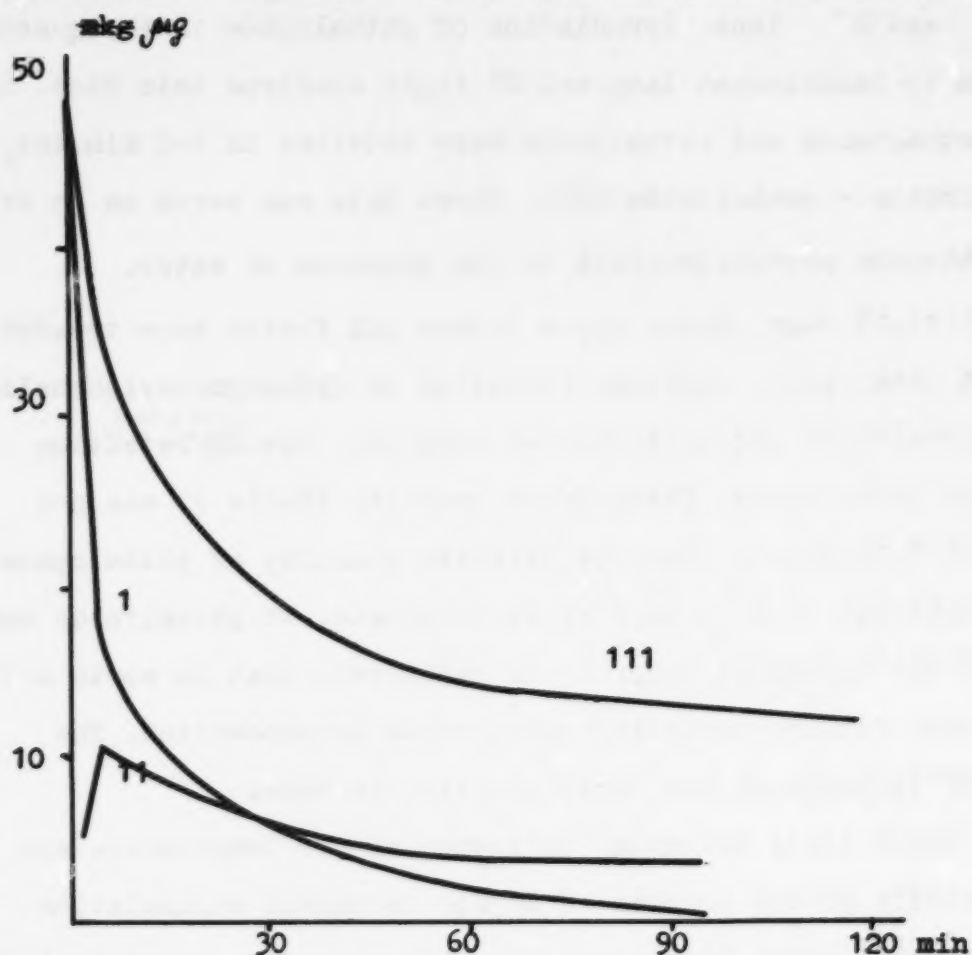


Fig.4 The kinetics curves of the alteration of Phthalophos and the formation of phthalimide under the action of UV-light.

I - phthalophos in water,  
 II - phthalimide in water,  
 III - phthalophos in the thinfilm.

It is to be noted that no oxygen analogue was detected when phthalophos was irradiated on thinlayer plates. No hydroxymethylphthalimide and phthalimide formation took place in the process of film irradiation. This suggested the possibility that they were formed in the presence of  $\text{OH}^-$  and  $\text{H}^+$  ions. Irradiation of phthalophos in an aqueous solution by luminiscent lamp and UV light confirms this fact. Hydroxymethylphthalimide and phthalimide were detected in 1-2 minutes, and in 10 minutes - phthalimide only. These data can serve as an evidence of phthalophos photohydrolysis in the presence of water.

The field test, where apple leaves and fruits were treated with 50% phthalophos, confirms formation of hydroxymethylphthalimide, phthalimide and unidentified compound, having <sup>greater</sup> retention time than phthalimide. Phthalimide quantity (Table 2) was not more than 0,01-0,02 % from the detected quantity of phthalophos in the interval of 3-15 days after treatment. No phthalimide was found in the harvested crop. It is hydrolysis that is worth noting among other factors promoting phthalophos decomposition. The effect of temperature and precipitation is less.

In model tests essential influence of air temperature and soil humidity on the process of sayfos (menazen) accumulation on pea plants, grown from seeds treated by sayfos, was revealed under controlled conditions. Moderate temperatures, sufficient moisture promote the compound penetration from treated soil to plants (Table 3). Under sunlight influence sayfos oxygen analogue is formed on surfaces of treated plants. On the 25th day its quantity exceeds sayfos content.

Table 2

The dynamics of phtalophos and phtalimide on the apples

| Days :<br>following<br>treatment: | Found             |                   |
|-----------------------------------|-------------------|-------------------|
|                                   | phtalophos, mg/kg | phtalimide, mg/kg |
| 0*                                | 4,3               | -                 |
| 1                                 | 3,9               | 2,0               |
| 2                                 | 4,4               | 5,6               |
| 3                                 | 4,0               | 8,8               |
| 7                                 | 2,7               | 5,4               |
| 10                                | 2,5               | 2,6               |
| 15                                | 2,0               | 1,1               |
| 24                                | 0,5               | 0,4               |
| 36                                | 0,1               | -                 |

\* two hours after treatment

The influence of soil characteristics and moisture on atrazine and prometryne persistence time was studied in 5 types of soil with different organic matter content, pH value and absorption capacity. The levels of complete moisture capacity were 45, 60 and 75%. At equal moisture level atrazine persistence depended on soil characteristics. Thus, at 60% of field moisture capacity - 78-81% of herbicide was inactivated in typical, lixivated and common black earths, 66% - in grey forest soil. It was soil moisture that was responsible for the atrazine persistence time. At 75% of field moisture capacity 78-93% of the compound was inactivated in black earths, at 45% - 52-61%. At



Table 3

Influence of the soil humidity and temperature on the  
sayfos content in plant

| The soil humidity<br>(% absolute)               | Temperature, °C, |       | Average by fac-<br>tor A,<br>LSD <sub>05</sub> = 1,07 |
|-------------------------------------------------|------------------|-------|-------------------------------------------------------|
|                                                 | 33-12            | 40-20 |                                                       |
| 18                                              | 5,47             | 2,11  | 3,79                                                  |
| 25                                              | 7,94             | 2,40  | 5,17                                                  |
| 37                                              | 16,74            | 6,48  | 11,61                                                 |
| Average by factor B<br>LSD <sub>05</sub> = 1,94 | 10,95            | 3,66  | 6,86                                                  |

the same time soil characteristics didn't influence prometryne persistence. At 60% of field moisture capacity - 91-97% was inactivated for 3 months in all kinds of soil. Besides, 2 months were needed to complete prometryne inactivation at 75% of field moisture capacity and a little bit more than 5 months - at 45%.

In field tests on maize simazine, atrazine, polytriazine and agelon residue range was 0,06 mg/kg of soil at the end of vegetation period, depending on the precipitation quantity and intensity in the stratum of 0-10 cm. Autumn and winter periods were characterized by herbicide redistribution from the upper stratum (0-10 cm) to the depth of 40 cm with the residue of 0,05-0,11 mg/kg of the soil.

STUDIES OF THE BEHAVIOUR OF ORGANOPHOSPHOROUS  
INSECTICIDES IN SOIL AND IN SOIL-PLANT SYSTEM

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Now in the Soviet Union organophosphorous insecticides (chlorophos, carbophos, phosphamid, gardona, syfos, methilnitrophos and its analogues metathion, sumithion, folithion et al.) which penetrate directly or indirectly into soil are widely used in agriculture for plant protection against Arthropoda. In connection with it studies of the behaviour of these insecticides in soil and also in soil-plant system are of great interest both for proper rational use of these chemicals for integrated control methods in plant protection and for the solving of toxicologohygienic problems.

As it is known the insecticidal conversion in soil and in plants is the process depending on many factors and changing under the influence of biological and nonbiological conditions.

Considering the factors as a system determining the character of the insecticidal behavior in biological objects, it should be

noted that of particular importance are:

a) physical and chemical properties of the pesticide characterizing the chemical by the stability of not only its original forms but also of its conversion products, as well as by its solubility in different environments, volatility, diffusion rate, persistence in different environments and so on;

b) methods of pesticidal use for the control of plant pests in agriculture;

c) environmental conditions (temperature, precipitations, solar radiation, air motion and so on);

d) soil features (its type and structure, the content of organic substances, pH value, the aggregation rate and so on) and plant peculiarities (anatomy-morphological, physiologico-biochemical ones).

A great number of papers elucidating the importance of nonbiological factors in the process of pesticidal conversion was published for last years (NOVOZHILOV, PETROVA, 1974; MEDVED, 1974, WAINTRAUB, 1974; KLISSENKO, 1975, O'BRIEN, 1975, FUKUTO, CROSBY, 1975 et al.). Over 20 reports were only dedicated to this problem at the 3rd International Congress on Chemistry of Pesticides which was held in Helsinki in 1974.

The majority of researchers considers physico-chemical characteristics of pesticides to be one of the main factors of their conversion.

Our researches and the analysis of modern scientific literature on this problem convince us that physico-chemical characteristics of the pesticide, UV-rays and humidity (precipitations) within first days after crop treatment with the chemical indeed are main indices in the system of factors of non-biological nature. Model experiments in chambers with artificial climate corroborate insignificant influence of temperature and illumination (with the exception of UV-spectrum part) on the rate of OFI destroying.

So, on the 10th day syfos content was the same when temperature was  $28^{\circ}\text{C}$  and illumination -  $300\text{ watt/m}^2$  and  $500\text{ watt/m}^2$ , that made up 34-35% from the original amount of the pesticide; when illumination was  $400\text{ watt/m}^2$  and  $t^{\circ} 20^{\circ}$  and  $30^{\circ}$  the toxicant content was 37-36%, respectively from its original amount.

The distribution of OFI in plant-soil-plant system is also connected with physico-chemical characteristics. It is noted that watersoluble insecticides are washed off by water and they are translocated from one system to another one, as for example, chlorophos. Chemicals scarcely soluble in water (carbophos, syfos, gardona et al.) are washed off only within the first day after a plant treatment. The distribution of Gardona in plants and in soil after spraying pea plants is shown in Table I. The majority of organophosphorous insecticides penetrating into the soil was found in maximum at the depth of



0-3 cm under the conditions of normal moistening for loam and chernozemic soil.

Table I

DISTRIBUTION OF GARDONA IN PLANTS AND IN SOIL

| Days after treatment | Gardona content(mg/kg) in |                |                         |                |                      |             |
|----------------------|---------------------------|----------------|-------------------------|----------------|----------------------|-------------|
|                      | upper part of the plant   |                | lower part of the plant |                | in the depth of soil |             |
|                      | one treatment             | two treatments | one treatment           | two treatments | 0 - 3 cm             | 3 - 10 cm   |
| 0                    | 14,9 ± 1,2                | 16,2 ± 1,25    | 2,1 ± 0,25              | 6,0 ± 0,2      | 1,15 ± 0,1           | 0,57 ± 0,1  |
| I                    | 12,0 ± 1,4                | 14,0 ± 1,4     | -                       | 4,0 ± 0,1      | 1,03 ± 0,1           | 0,5 ± 0,03  |
| 4                    | 8,2 ± 0,9                 | 7,8 ± 0,96     | -                       | 2,1 ± 0,1      | 0,45 ± 0,05          | 0,25 ± 0,01 |
| 8                    | 5,0 ± 0,15                | 2,9 ± 0,3      | 0,56 ± 0,1              | 0,96 ± 0,09    | 0,22 ± 0,05          | 0,11 ± 0,01 |
| II                   | n. d.                     | 1,3 ± 0,2      | n. d.                   | 0,48 ± 0,1     | 0,4 ± 0,1            | 0,21 ± 0,01 |
| 15                   | n. d.                     | 0,93 ± 0,1     | n. d.                   | 0,43 ± 0,05    | 0,2 ± 0,07           | n. d.       |

The method of OFI application exerts a significant effect on their dynamics. The product applied into soil (as dust or granules) is found in growing plants within 2 - 4 months (Tables 2, 3, 4), whereas for the sprayed insecticide it was found within 0.5 - 1.5 months (Table 5).

Studies of <sup>the</sup>syfos behaviour under field conditions of the Leningrad region allowed to ascertain that half-life period of syfos in pea and potato plants was 3-5 days for vegetation plant spraying. The decrease of syfos content up to the level of permissible residues in the USSR occurs in 5-7 days; the



Table 2

DYNAMICS OF CHLOROPHOS IN PLANTS AND IN SOIL

| S A M P L E                        |        | Chlorophos content (mg/kg) |         |         |         |         |         |          |          |          |
|------------------------------------|--------|----------------------------|---------|---------|---------|---------|---------|----------|----------|----------|
|                                    |        | 7 days                     | 15 days | 30 days | 45 days | 60 days | 90 days | 100 days | 120 days | 140 days |
| Clover<br>(Trifolium)              | roots  | 25                         | 20      | 2,2     | 1,4     | 0       |         |          |          |          |
|                                    | leaves | 15                         | 13,5    | 1,2     | 0,3     | 0       |         |          |          |          |
| Cabbage<br>(Brassic <sub>a</sub> ) | leaves | 112                        | 80      | 26      | 11,4    | 3,3     | 1,2     | 0,8      | 0,2      |          |
| S o i l                            |        | 534                        | 241     | 59,0    | 18,3    | 4,2     | 1,8     | 1,0      | 0,6      | 0        |

x) 150 kg/ha 7% toxic granules of chlorophos were applied into soil in May.

Table 3

SYFOS AMOUNTS IN PEA PLANTS AFTER SEED TREATMENTS (2 kg/100 kg seed)1974

| <u>T e s t<br/>v a r i a n t</u> | Syfos content (mg/kg),<br>days after treatments |     |     |     |            |               |
|----------------------------------|-------------------------------------------------|-----|-----|-----|------------|---------------|
|                                  | i n   p l a n t s                               |     |     |     |            | i n   s o i l |
|                                  | 30                                              | 40  | 50  | 60  | 75         | 75            |
| In field .....                   | 5,1                                             | 2,7 | 0,1 | No  | -          | No            |
| In glasshouse..                  | 5,7                                             | 3,5 | 0,5 | 0,2 | 0,15 - 0,1 | 0,01          |

Table 4

SYFOS DYNAMICS IN PEA PLANTS AND IN SOIL AFTER SEED TREATMENTS

1976

| Sample | Application rates<br>(kg./100 kg. seed) | Syfos content (mg/kg),<br>days after treatment |     |     |     |     |     |     |     |     |     |
|--------|-----------------------------------------|------------------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|        |                                         | 20                                             | 30  | 35  | 40  | 45  | 50  | 55  | 60  | 65  | 80  |
| plants | 2                                       | 10,0                                           | 6,7 | 4,5 | 4,0 | 2,2 | 2,1 | 2,0 | 2,0 | 1,3 | 0,4 |
|        |                                         | 1,9                                            | 1,5 | 0,9 | 0,9 | 0,7 | 0,6 | 0,6 | 0,6 | 0,5 | 0,4 |
| plants | 3                                       | 13,5                                           | 8,2 | 4,2 | 4,1 | 3,9 | 3,5 | 3,0 | 2,3 | 2,0 | 0,9 |
|        |                                         | 6,5                                            | 4,2 | 2,2 | 1,9 | 1,7 | 1,5 | 1,3 | 0,9 | 0,7 | 0,6 |

Table 5

SYFOS DYNAMICS IN PLANTS OF POTATO AND PEA DEPENDING  
ON THE NUMBER OF TREATMENTS 1975

(concentration of Syfos 0,1 % a. i. )

| Crop   | No. of<br>treatments | Syfos content (mg/kg),<br>days after treatment |     |     |     |     |     |     |      |      |
|--------|----------------------|------------------------------------------------|-----|-----|-----|-----|-----|-----|------|------|
|        |                      | 0                                              | 1   | 3   | 5   | 7   | 12  | 17  | 22   | 30   |
| Pea    | I                    | 2,5                                            | 1,6 | 1,0 | 0,8 | 0,7 | 0,4 |     | -    | -    |
| Potato |                      | 3,0                                            | 2,0 | 1,1 | 0,9 | 0,8 | 0,5 |     | -    | -    |
| Pea    | II                   | 4,0                                            | 3,5 | 3,0 | 2,0 | 0,5 | 0,5 | 0,1 | 0,01 | -    |
| Potato |                      | 4,2                                            | 3,6 | 3,1 | 1,5 | 0,9 | 0,6 | 0,2 | 0,01 | 0,01 |

product was found in the amount of 0.01 mg/kg within 30-35 days.

When pea seeds are treated with Syfos the toxicant penetrates into <sup>(the)</sup> serial parts of plants and remains there at 0.5 - 0.1 mg/kg level within 50 - 70 days depending on climatic factors. The rates of syfos <sup>content</sup> decrease in pea and potato plants are relatively constant and depend on the original insecticide content in them (Tables 3, 4, 5).

We consider the process of insecticidal conversion in a biological object (in the plant, in soil) as a function in the system of factors of biological and nonbiological nature. We emphasize first of all anatomo-morphological plant peculiarities in the system of factors, as the distribution of the toxicant in a plant is connected with them (Table 6).

Our researches with crops varying in the anatomo-morphological structure of leaves (pea, bean, tomato, cucumber and cabbage plants) have shown that the toxicant distribution directly depends on leaf hairness, wax content in the cuticle, lipids and other lipid-like substances and on their quality, too.

As it should be expected, leaves with significant hairness (cucumber, tomato plants) or a wax layer (cabbage plants) had a more considerable amount of the insecticide on their surface compared with pea and bean leaves. So the ratio of the "surface" carbophos to the absorbed one was 1 : 1 in leaves of cabbage and cucumber plants. This ratio was 1 : 1,5; 1:1,4

Table 6  
DISTRIBUTION OF ORGANOPHOSPHOROUS INSECTICIDES  
IN PLANT LEAVES

| Pesticide<br>Test Plants | Ratio of "surface" to "absorbed" insecticide |                      |           |           |
|--------------------------|----------------------------------------------|----------------------|-----------|-----------|
|                          | Metathion                                    | Methyl-<br>nitrophen | Sumithion | Carbophos |
| Tomato .....             | I : I                                        | I : 0,3              | I : 0,4   | I : 0,7   |
| Cucumber .....           | I : 0,8                                      | I : 0,3              | I : 0,4   | I : I     |
| Cabbage .....            | I : 0,7                                      | I : 0,7              | I : 0,7   | I : I     |
| Bean .....               | I : I,2                                      | I : I                | I : I     | I : I,5   |
| Pea .....                | I : I,5                                      | I : 0,9              | I : I     | I : I,4   |
| <u>Pea lines:</u>        |                                              |                      |           |           |
| Zelenozerny wax          | I : 0,8                                      | I : 0,6              | I : 0,7   | I : I     |
| Zelenozerny ..           | I : I,6                                      | I : I,3              | I : I,2   | 0,2 : I   |
| Acacia wax ...           | I : 0,6                                      | I : 0,4              | I : 0,6   | I : I     |
| Acacia emerald           | I : I, I                                     | I : I                | I : I     | 0, I : I  |

in leaves of pea and bean plants, respectively. It should be noted that the toxicant distribution in pea plants depends to a great extent on the presence or absence of cuticle waxes. The higher content of the "surface" insecticide is found in isogenic pea lines characterized by the presence of a wax gene (Zelenozerny wax, Acacia wax) as compared with unwax pea lines (Zelenozerny unwax, Acacia emerald).

The same regularity is also observed with other insecticides.

Since the degradation rates in the "surface" and the absorbed insecticide are different, the toxicant distribution

in plant leaves is undoubtedly of great importance in the process of detoxication.

The insecticide on epidermis surface (the "surface" insecticide) is mainly destroyed under the influence of factors of the nonbiological nature, <sup>whereas</sup> the toxicant penetrated into tissues ("absorbed" one) degrades under the influence of oxidation-reduction cell enzymes (Table 7) and hydrolytic ones (Table 8).

Table 7

OXICARBOPHOS FORMATION IN PEA LINES  
WITH DIFFERENT PEROXIDASE ACTIVITY

| PEA LINES        | Peroxidase activity<br>in mg of oxidized<br>pyrocatechol per 1 g<br>of protein | Oxicarbophos content,<br>formed from 100 mg<br>of absorbed carbophos<br>in mg |
|------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Zelenozerny wax  | 126                                                                            | 5                                                                             |
| Acacia wax ..... | 129                                                                            | 7                                                                             |
| M u l k .....    | 131                                                                            | 7                                                                             |
| Moscovsky .....  | 137                                                                            | 10                                                                            |
| Meistoschitz ... | 158                                                                            | 14                                                                            |
| Shamboy 180 ..   | 170                                                                            | 12                                                                            |
| Lincoln .....    | 170                                                                            | 16                                                                            |
| Senator .....    | 178                                                                            | 16                                                                            |
| Meteor .....     | 190                                                                            | 17                                                                            |



THE PRODUCTS OF THE HYDROLYTIC CONVERSION  
FOR CARBOPHOS AND METHYLNITROPHOS IN PEA PLANTS

| <u>The sample</u>     | Days after treatment | Carbophos metabolites |        | Methylnitrophos metabolites |                             |
|-----------------------|----------------------|-----------------------|--------|-----------------------------|-----------------------------|
|                       |                      | monoacid              | diacid | desmethyl-nitrophos         | dimethyl-thiophosphate acid |
| Lincoln x Karmazinovy | I                    | 5,3                   | 3,2    | I,5                         | I,4                         |
|                       | 5                    | -                     | 8,0    | 0,4                         | 0,1                         |
|                       | 14                   | -                     | -      | 0,1                         | -                           |
| Lincoln .....         | I                    | -                     | -      | 0,1                         | -                           |
|                       | 5                    | 2,2                   | -      | 14                          | 2,3                         |
|                       | 14                   | -                     | 5,1    | 0,5                         | traces                      |
| Karmazinovy .....     | I                    | -                     | -      | -                           | -                           |
|                       | 5                    | I,5                   | 3,3    | I,6                         | I,1                         |
|                       | 14                   | -                     | 5,0    | 0,2                         | 0,3                         |

As it is known, the formation of oxidized metabolites is connected with the activity of oxidation-reduction enzymes, in particular, with peroxidase. On this basis we studied the formation of oxicarbophos and oximethylnitrophos in pea lines with different peroxidase activity of this enzyme.

Table 7 shows that larger amount of oxidized metabolite is formed in lines with increased activity of peroxidase (Meteor, Senator, Lincoln) as compared with Mulk, Acacia wax, Zelenozerny wax with similar level of the "absorbed" insecticide.

Our studies with different plants in different periods of their development indicate that formation of oxidized forms of metabolites from "absorbed" metabolites occurs

under the conditions of the most active metabolism, in particular, in spring, and also within the first days after a plant treatment with the insecticide when defensive reactions mobilize in response to the incorporation of the substances which are not characteristic of the organism.

Products of toxicant hydrolytical degradation are formed in significant amounts along with oxidized forms. Their level correlates with the esterase activity, and the data obtained for the separate lines and the interline hybrids confirm it.

On the first day the products of hydrolytical insecticidal conversion were already observed in the hybrid pea form with the higher esterase activity, compared with the parent lines where they appeared 5-7 days later.

Complex of the factors affecting the process of pesticidal detoxication was studied in the wide scale under field conditions with gardona.

Data on toxicant distribution in different plant parts and in soil were obtained (Table 9): 85.3% of the insecticide were found in upper plant layer in 2 hours after a treatment with gardona; 10.8% of Gardona was found in lower layer, 3.5% - in soil, and 81.7%, 15.2% and 3.1%, respectively, in 5 days.

As we see, the larger amount of the insecticide is found in the upper part of the pea plant, and only 2-3% of the toxicant penetrate into soil.

Table 9

DISTRIBUTION OF GARDONA IN PEA PLANTS AND IN SOIL

(Spraying according to measure system, recommended in the control  
of pea pests under the conditions of Chernovitsy region)

| Year,<br>number of treatments | Gardona content (mg/kg) in |                      |                 |             |
|-------------------------------|----------------------------|----------------------|-----------------|-------------|
|                               | upper part of plants       | lower part of plants | soil (0 - 3 cm) |             |
| 1973                          | One treatment              | 14,9 ± 1,2           | 2,1 ± 0,25      | 1,15 ± 0,15 |
|                               | Two treatments             | 16,2 ± 1,25          | 1,65 ± 0,2      | 1,7 ± 0,20  |
| 1974                          | One treatment              | 13,1 ± 1,6           | 6,0 ± 0,2       | 0,6 ± 0,07  |
|                               | Two treatments             | 15,9 ± 1,4           | 3,7 ± 0,2       | 1,20 ± 0,11 |

This regularity is valid for all the years when the experiments were carried out. Similar data were also obtained for the other crops. Our research into the significance of the factors in detoxication process will provide an opportunity to substantiate prediction of pesticide residues in biological objects, and in connection with it, to solve properly the practical problems of rational use of chemicals.

## METABOLISM OF PYRETHROID INSECTICIDES AND THIOCARBAMATE HERBICIDES

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### ABSTRACT

Knowledge of the metabolism of pesticides contributes to an understanding of their mode of action, selective toxicity, and residual persistence. It also assists in the discovery of compounds with increased potency and safety. Investigations at Berkeley with pyrethroid insecticides and thiocarbamate herbicides using mammals, insects, plants and enzyme systems illustrate these points.

### PYRETHROIDS

Synthetic pyrethroids are possible replacements for chlorinated hydrocarbons and other insecticides that lack appropriate toxicological and persistence characteristics.

The first definitive step in understanding pyrethroid metabolism came from studies on S-bioallethrin, pyrethrin I and other chrysanthemates with housefly monooxygenase enzymes that showed the lability of the trans-methyl group of the isobutenyl moiety (Fig. 1) (1-3). These studies also: 1) showed that methylenedioxyphenyl synergists for pyrethroids block the enzyme-

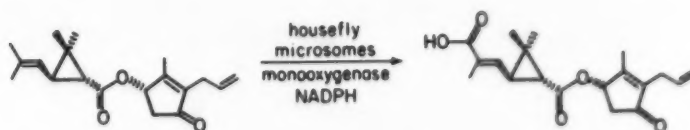


Fig. 1. Metabolism of S-bioallethrin by the housefly microsomal monooxygenase system (1-3)

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tic oxidation; 2) stimulated others to prepare potent pyrethroids by replacing the isobutenyl moiety with less biodegradable substituents; and 3) suggested the pathway later found to exist in Chrysanthemum cinerariaefolium for biosynthesis of pyrethrin II.

Metabolic pathways for pyrethrin I, pyrethrin II and S-bioallethrin in rats were defined by isolation of the [ $^{14}\text{C}$ ]- or [ $^3\text{H}$ ]metabolites and identification by nuclear magnetic resonance and mass spectrometry (Fig. 2) (4-8). Major sites of oxidative attack are at the alcohol side chain,

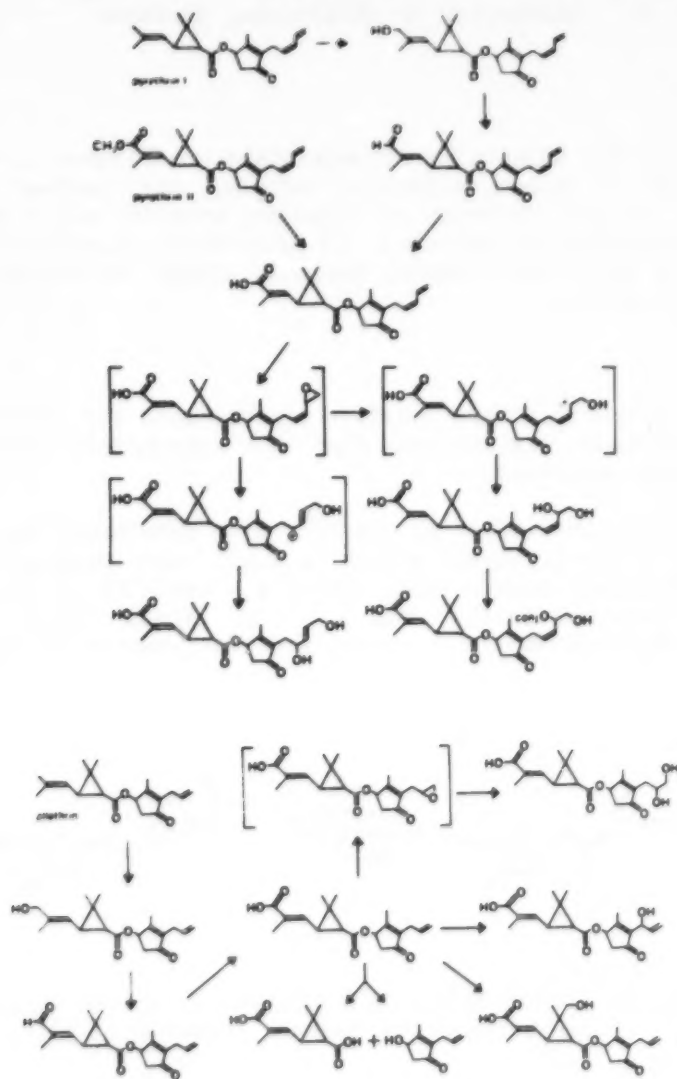


Fig. 2. Metabolism of pyrethrin I, pyrethrin II and S-bioallethrin by rats (4-8)



the isobutenyl moiety and the geminal-dimethyl group. There is little or no hydrolysis of the cyclopropanecarboxylate ester group.

Bioresmethrin (1R,trans-resmethrin) is a photolabile but highly potent insecticide. It has an extremely low acute toxicity for mammals whereas the 1R,cis-isomer is more toxic. Mouse liver microsomes hydrolyze 1R,trans-resmethrin much more rapidly than 1R,cis-resmethrin (Fig. 3) (9-14). On

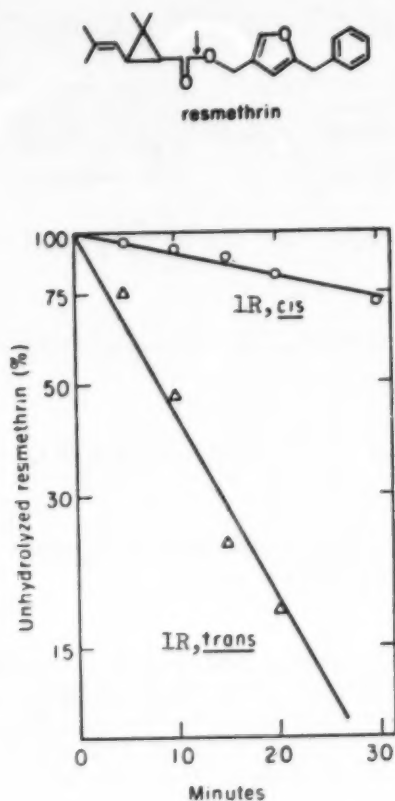


Fig. 3. Metabolism of 1R-resmethrin by mouse liver microsomal esterases (9-14)

a more general basis, they hydrolyze trans-cyclopropanecarboxylic acid esters with primary alcohols at a much greater rate than they hydrolyze the corresponding cis-esters with primary alcohols or the trans-esters with secondary alcohols.

Permethrin no longer has the biodegradable and photolabile substituents present in earlier pyrethroids. The 1R,trans- and 1R,cis-isomers are metabolized in rats by ester hydrolysis and hydroxylation of the geminal-dimethyl group and the phenoxy ring (Fig. 4) (15,16). The cis-isomer is more persistent than the trans-isomer because of the large rate difference in ester hydrolysis.

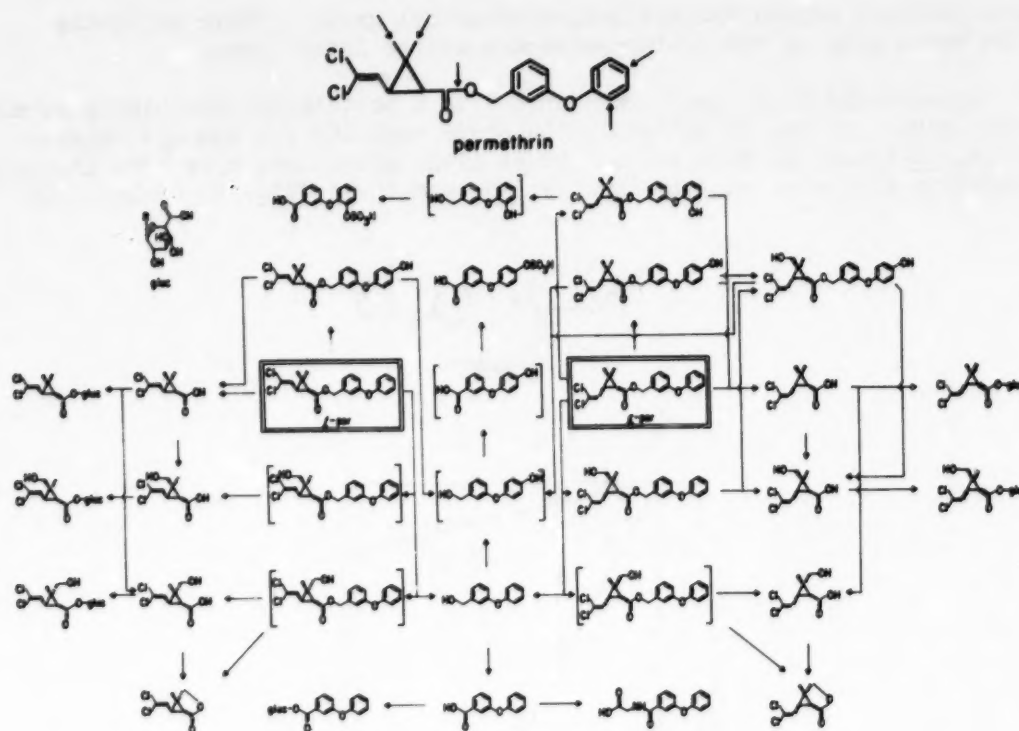


Fig. 4. Metabolism of 1R,trans-permethrin (t-per) and 1R,cis-permethrin (c-per) by rats (15,16)

Mouse liver microsomal oxidase and esterase systems were used to examine the structure-biodegradability relationships of 44 pyrethroids. Introduction of an  $\alpha$ -cyano substituent in the alcohol to increase the insecticidal potency leads to compounds (NRDC 149 and S-5602) that are both slowly hydrolyzed and slowly oxidized (Fig. 5) (14).

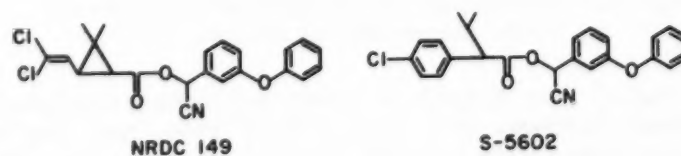


Fig. 5.  $\alpha$ -Cyano pyrethroids resistant to metabolism by mouse liver microsomal monooxygenase and esterase systems (14)

Stereospecificity is sometimes encountered in the preferred site of monooxygenase attack. For example, the geminal-dimethyl group of 1R,trans-

permethrin is oxidized by mouse and rat liver enzymes specifically at the cis-methyl group while the 1S,trans-isomer is oxidized only at the trans-methyl group (Fig. 6) (17). Oxidation of the geminal-dimethyl group in the 1R- and 1S,cis-isomers is less specific.

The continuing studies are examining new pyrethroids and a greater variety of organisms (cows, chickens and various insect species).

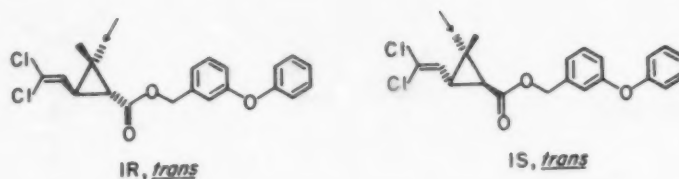


Fig. 6. Stereospecificity in mouse liver microsomal monooxygenase metabolism of 1R,trans- and 1S,trans-permethrin (17)

#### THIOCARBAMATES

Thiocarbamate herbicides were previously reported to undergo hydrolysis and further metabolism of the mercaptan and amine in mammals and plants. In contrast, the present studies show the importance of non-hydrolytic pathways for thiocarbamate metabolism.

Investigations with mouse liver enzymes establish that thiocarbamates undergo microsomal monooxygenase attack to form the sulfoxide and N-dealkyl derivatives. The sulfoxide is then rapidly cleaved by the GSH S-transferase system, forming the GSH conjugate (Fig. 7) (18-20). Further metabolism of the GSH conjugate in rats yields the cysteine conjugate and a variety of other metabolites including the mercapturic acids (Fig. 7) (21,22). An additional but undefined pathway in rats does not involve the sulfoxide intermediate in cleaving a portion of the thiocarbamate dose (22).

The thiocarbamate sulfoxides are also formed in plants and are usually more potent herbicides and often cause less crop damage than the corresponding thiocarbamates (Table 1) (18,20). This suggests that the sulfoxide metabolites may be the actual herbicides. The sulfoxides may act by carbamoylating a critical thiol site important in lipid biosynthesis (Fig. 8) (20,21,23).

Sensitive corn varieties are protected from thiocarbamate injury on adding an "antidote", such as N,N-diallyl-2,2-dichloroacetamide. The antidote elevates the level of GSH and increases the activity of the GSH S-transferase so the thiocarbamate sulfoxides are more readily detoxified by carbamoylation of GSH (Fig. 8) (21-23). Many related antidotes for thiocarbamate injury appear to act in the same way. Thus, the antidote builds a resistance mechanism into susceptible varieties of corn.

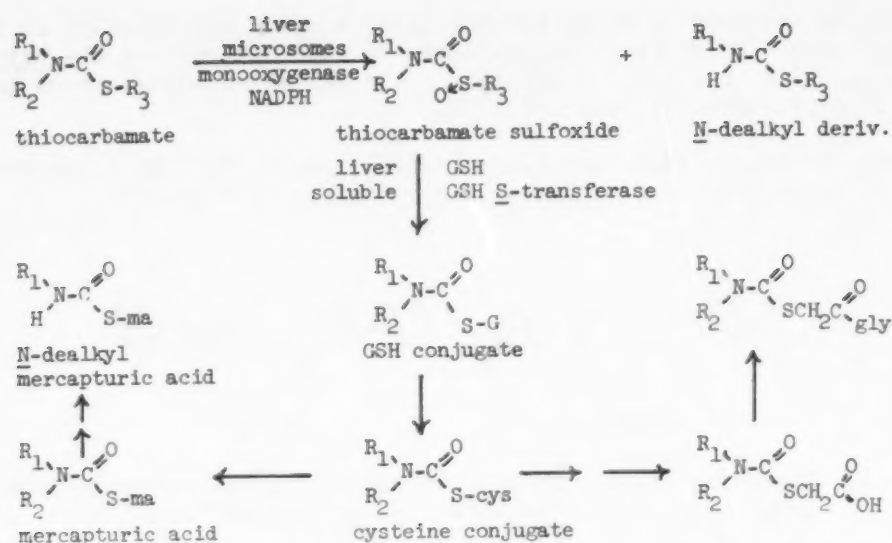


Fig. 7. Metabolism of thiocarbamates in rats. Abbreviations:  $R_1$  and  $R_2$  = alkyl or cycloalkyl;  $R_3$  = alkyl or substituted-benzyl; GSH = glutathione; G, cys and ma = S-derivatives of GSH, cysteine and N-acetyl cysteine (mercapturic acid), respectively; gly = N-derivative of glycine (18-22)

Table 1. Herbicidal activity and crop injury with EPTC, butylate and their sulfoxides when mixed with the soil before the seeds were planted (18,20).

| Plant               | Herb.<br>rate,<br>kg/ha | Injury rating, ave. % |                   |          |                       |
|---------------------|-------------------------|-----------------------|-------------------|----------|-----------------------|
|                     |                         | EPTC                  | EPTC<br>sulfoxide | Butylate | Butylate<br>sulfoxide |
| <u>Weed species</u> |                         |                       |                   |          |                       |
| 3 Broadleafs        | 0.5                     | 58                    | 90                | 23       | 68                    |
| 10 Broadleafs       | 1.7                     | 92                    | 98                | 55       | 99                    |
| 5 Grasses           | 0.5                     | 94                    | 89                | 56       | 98                    |
| <u>Crops</u>        |                         |                       |                   |          |                       |
| Corn                | 3.4                     | 70 <sup>a</sup>       | 0 <sup>a</sup>    | 0        | 0                     |
| Sugarbeet           | 3.4                     | 98                    | 99                | 20       | 90                    |
| Field bean          | 3.4                     | 10                    | 0                 | 80       | 20                    |
| Cotton              | 3.4                     | --                    | --                | 40       | 100                   |

<sup>a</sup>With a susceptible corn variety, the EPTC injury rating was 94 and 100% at 6.4 and 27 kg/ha, respectively, whereas no injury resulted with these rates of EPTC sulfoxide.

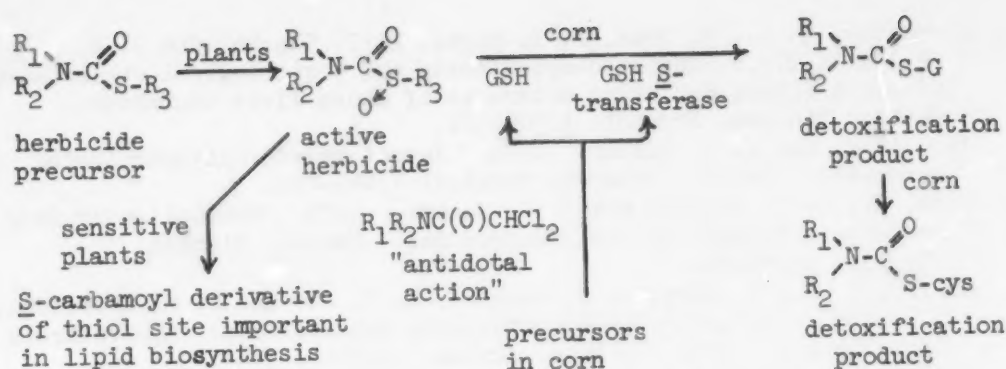


Fig. 8. Metabolism of thiocarbamates in plants and the action of dichloroacetamide "antidotes" in corn (18,20-23)

#### ACKNOWLEDGMENT

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**BASIC TRENDS AND RESULTS  
IN THE STUDY OF PESTICIDE  
TOXICOLOGY**

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The discovery of chemical means of protection of plants against pests and plant diseases,-pesticides, is an outstanding achievement of contemporary science. Pesticides hold an important part in the reduction of harvest losses. Along with it pesticides possess certain qualities which present potential dangers for public health. Of these mention should be primarily made of the high biological activity of pesticides, the ability to survive in the environment for lengthy periods, to accumulate in foodstuffs. The distribution of pesticides on huge territories, penetration into soil, water reservoirs, plants and animals create real conditions for the penetration of these agents into the human organism.

The above listed features of pesticides make it necessary in the hygienic and toxicological estimation of them to take into account all the consequences which may arise from their use.

The adverse effect of pesticides may develop in various directions. They may be the causes of acute poisoning. 34 thousand cases

of acute poisoning with pesticides have been described in world literature (1). Poisoning can be prevented by correct organization of work, adherence to cautionary measures. It is much more difficult to prevent chronic poisoning. Of great danger in this respect are stable pesticides, especially chloroorganic compounds. It is well known that many chemical substances passing to the organism for long periods in small doses may not induce clearly expressed signs of poisoning. However, they can affect the immunobiological reactivity of the organism, reduce its resistivity to the effect of various pathogenic factors. And this should also be taken into account in estimating pesticides. Finally, chemical substances may contribute to the appearance of a number of pathologic processes which are not confined to the concept of "intoxication" but which in their after-effects may be much more serious than intoxication. The question is about the appearance of allergic states, malignant growth, about the mutagenous, teratogenic, embryotoxic and gonadotoxic effect of chemical substances. These problems must also be studied in examining pesticides.

One of the main problems of toxicology is to obtain data concerning toxicity and other noxious properties of pesticides prior to their introduction into practice. This principle is fully realized in the USSR. No substance is allowed to be used as a pesticide without preliminary studies, following which it can be sanctioned to use by the Central Sanitary and Epidemiologic Board of the Ministry of Health of the USSR.

The following measures are used to accelerate toxicologic studies: (a) carrying out the research in stages, (b) compulsory experimental toxicological and hygienic examinations, (c) a number of criteria are given required for toxicological examinations and hygienic standardization of preparations, (d) concrete methods of analysis are recommended. The stage approach to the examinations enables the decision to be made at the very beginning about expediency of the further analysis of a substance in case of its high toxicity. Thus highly toxic organophosphorous pesticides as tetraethylpyrophosphate (TEPP), thymet, M-74, chlorinated hydrocarbonates of the diene synthesis (dieldrin, endrin, isodrin and many others). In case of a favourable appraisal of the preparation at the second stage, examinations are made aimed at the substantiation of limiting concentrations in the working zone air, atmospheric air, foodstuffs and in water, the working conditions during pesticide tests in agriculture are studied and prophylactic measures are worked out. If a decision is made to produce the new pesticide commercially, then the physiologic and biochemical mechanisms of its action are studied fundamentally and specific measures of prophylaxis and therapy of poisoning are elaborated.

The unification of the research program aimed at solving specific problems associated with toxicological appraisal and hygienic standardization of new chemical substances, the strict stage-by-stage approach to the research makes it possible not only to solve practical problems in short periods but also <sup>to</sup> contribute to the accumulation of data on certain theoretical questions.



Now more than 900 chemical compounds are used in the world as pesticides of which about 250 are either used or tested in the USSR; however, since some of them contain one and the same active agents, there are much less individual chemical substances of this kind (2). The comparison of the range of pesticides in use for a number of years bears testimony to a rapid increase in their nomenclature connected with the growing stability of pests to certain preparations, necessity of their replacement and alteration, with the trend to use pesticides selectively affecting noxious objects without injuring the useful ones, having low toxicity for people and animals, and with a number of other reasons (3-7).

The present report deals only with some most important trends in the toxicological study of pesticides and considers findings obtained in recent years which characterize the potential dangers of pesticides related to the two most widespread classes, viz. chlororganic and organophosphorous compounds; due attention is also given to the ways of preventing their unfavourable effect on public health'.

It has been proved beyond doubt that DDT is accumulating in the adipose tissue of most people of the world.

It has been established that along with DDT other chlororganic pesticides such as Lindane, dieldrin, heptachlor are also accumulating in the adipose tissue but their content is considerably lower than DDT and commonly does not exceed 0.1-0.3 mg/kg. Different contents of DDT in foodstuffs, peculiarities of food rations (consumption of meat, dairy products, etc.) are perhaps the main reason



for different contents of the insecticide in the adipose tissue of people (8-12).

The question about the carriage of DDT and other chlororganic pesticides is no longer a subject for debate. The harmfulness of this carriage is still under discussion. In recent years new experimental and clinical findings have been obtained bearing evidence to harmfulness of the carriage of chlororganic compounds (13-32).

The effect of small doses of DDT to the functional state and structure of liver has been established (22). Prolonged administration of DDT to laboratory animals increases their sensitivity to coronary spastic agents (pituitrin), accelerates the development of experimental cholesteric atherosclerosis in rabbits (23-25). It has been proved that DDT affects the intensity of energy metabolism, the fixation and release of serotonin, the content of pyridine nucleotides in animal tissues, the permeability of cell membranes, the immunohematologic indices (27-32).

In the general appraisal of the potential danger of DDT due attention should be paid to the effect of small doses of DDT on the endocrine system of animals, and, which is of particular importance, to the gonadotoxic, mutagenous and carcinogenic effect of DDT (33-36). In one of the experiments (34) five generations of inbred mice were kept on a ration with the addition of DDT, and starting with the second generation the rate of malignant tumors (carcinoma and sarcoma) increased (28.7% cases as against 3.2% in the controls), and the number of leukemia cases increased, starting from the third generation. The carcinogenic effect of DDT has been confirmed by the study of V.S.Turussov (37).

All the mentioned information related to the harmfulness of DDT makes it necessary to speed up the research work aimed at the replacement of it and other stable chlororganic pesticides in agriculture.

The existence of a number of adverse properties in chlororganic pesticides has led to a vast development of toxicological research of less stable and less cumulative organophosphorous compounds. Their high toxicity for people and warm-blooded animals was the principal obstacle to the wide use of such compounds. Information related to the acute poisoning of people by compounds of this group has been reported and is being published (1, 38, 39). The danger of chronic poisoning by OPC has been studied to a considerably lesser extent, (40, 41).

A number of efficient substances have been found among OPC with medium (chlorophos, carbophos, threechlormethaphos-3, methyl-nitrophos, methathion, bytex, dibrom, amiphos, cyanox and others) and low (sajphos, gardona, bromophos, abat, valexon, demuphos) toxicity for warm-blooded animals and man. The feasibility of acute poisoning from these preparations is considerably less in comparison with mercaptophos and thiophos used before, as well as with methyl-mercaptophos, methaphos, phosphamide and others still used in agriculture. Toxodynamics of these compounds is being studied at present.

In recent years information has been reported related to the possibility of the injurious effect of organophosphorous preparations on the fetus and fetation. It has been established that parathion, methylparathion, dichlophos, diazinon, and TEPP penetrate the

placenta of rats and cause a frequent resorption of the fetus, a reduction in the fetus weight and the weight of placenta, as well as congenital malformation. Certain preparations (parathion, diazinon, TEPP) brought about a resorption of the fetus when administered in doses which did not cause intoxication of the pregnant animals (42-47).

The embryotoxic effect of phthalophos has been established also with comparatively low dosage (administered in pregnancy every other day in 0.3 mg/kg - 1/500 part of the lethal dose) (48). A distinct dependence of the pronounced character of the phthalophos embryotoxic properties on the rate of daily dose has been found. A single administration of higher doses of phthalophos may bring about a teratogenic effect (flipper-like extremities, strangulation of the pelvic girdle, hydrocephalus, hydronephrosis). When phthalophos is administered to pregnant rats, it can be found together with its metabolite (phthalimide) in small concentrations in the uterus, placenta and fetus tissues. It has been established that the embryotoxic effect also manifests itself due to the introduction of phthalimide which is the phthalophos metabolite (48).

On the basis of the finding it could be assumed that the embryotoxic effect is associated not with the organophosphorous compound itself but with the phthalimidic part of its molecule which also enters into the composition of the well known thalidomine teratogen.

However, recently convincing facts have been obtained about the availability of genadotoxic, embryotoxic and teratogenic properties in chlorophos and methylmercaptophos in the absence of the phthali-

side group (44-47,49). A substantial change in the fertility of rats has been discovered caused by the inhalation of methyl-mercaptophos. It has been ascertained that methylmercaptophos in small doses enhances the motor activity of the uterus of pregnant animals (49).

A report has been appeared about the carcinogenic effect of chlorophos which was revealed in the experiment on the Vistar rats and on mice of the AB strain (50). The authors associate this effect with alkylic properties in chlorophos. At present the mutagenous properties of organophosphorous pesticides are being studied.

All those findings indicate that the information concerning the acute toxicity of organophosphorous pesticides is insufficient for their appraisal. An all-round examination is required of the pesticides to rule out their adverse effect on the progeny and other remote after-effects.

A new approach to the directional synthesis of organophosphorous pesticides and acaricides has been realized in the laboratory of Academician M.I. Kabachnik(51-54). Various OPC containing radicals of natural aminoacids in the molecule have been synthesized. It was suggested that the presence in the OPC molecule of amino acid radicals could affect the character and speed of inhibition of choline-sterases of warm-blooded animals and insects. The structure of the amino acid can also have influence on the interaction of OPC with enzymes, providing for their detoxication, particularly, with carboxyl-esterases and peptidases. These theoretical assumptions have been justified. A number of organophosphorous pesticides, low-toxic for warm-blooded animals and possessing a selective insecticidal and acaricidal effect,



have been synthesized. The examination of these compounds has made it possible to ascertain the relation between the features of their structure, character and the rate of metabolism, by the interaction with cholinesterase to clarify the role of steric factors in the reaction with carboxylesterases. It is important that these compounds disintegrate into natural metabolites which lessens the likelihood of the appearance of unfavourable after-effects.

New results have been obtained in the study of the mechanism of action of OPC (55-57) and of cholinesterase reactivators which can be used as antidotes of organophosphorous pesticides (58-63).

Combining histochemical, electronic microscopy and electrophysiological (micropotentials) methods of analysis, we succeeded in proving that not only the activation of cholinesterase but also the influence of the reactivators on the functioning of pre- and postsynaptic formations are of importance in the mechanism of action of OPC and diproxime (TMB-4) (59, 63).

Proceeding from the hypothesis that reactivators close in structure to acetylcholine can better reactivate cholinesterase, we synthesized a series of S-diethylaminoethyl ethers of thiohydroxirane acids some of which turned to be active antidotes of organophosphorous pesticides (60-63).

In the USSR there is an orderly system of the toxicohygienic appraisal of pesticides which enables both the problems of pesticide introduction into farming practice and of hygienic regulation to be solved in due time. Rules are laid down for the sequence



and periods of examining the toxic properties of pesticides entering the organism by various routes, for the conditions and duration of experiments on the study of the cumulative effect of substances, for the duration of chronic experiments, for the conditions of experiments aimed at revealing the gonodotoxic, embryotoxic, teratogenic, mutagenic and allergenic properties of pesticides. The analysis of pesticides should be carried out in such a manner as to establish their potential and real dangers which may be dependent not only on the toxic properties, but also on the ability to cause any pathogenic effect. Since it takes much work and time to reveal allergenic, mutagenic, gonadotoxic, embryotoxic, teratogenic and particularly blastomogenic properties in substances, new pesticides should be analyzed in stages.

If a preparation is recommended for pilot-plant production, toxico-hygienic studies must be carried out in full scope and end in the establishment of hygienic standards and norms for the content of pesticides in the environmental objects (working zone air, atmospheric air, foodstuffs, water of water reservoirs).

The hygienic standards must guarantee against any adverse effect of pesticides on the health of man, and therefore in establishing the standards the possible remote unfavourable after-effects must be taken into account.

For practical decisions about the possibility and scope of use of pesticides, as well as about their hygienic standardization of much importance is the elaboration of quantitative criteria of harmfulness on the basis of which the pesticide can be related to

one or another group of hygienic classification, and the hygienic standards can be determined (6).

It should be stressed that there is an ever growing trend to estimate the connection of the revealed changes with the duration of the effect, to ascertain the probable threshold levels of the effect of substances possessing a specific action or able to cause remote after-effects. Along with the quantitative aspect of the problem due attention is given to qualitative aspects such as the study of biochemical and structural changes which determine the development of pathological processes.

We consider<sup>as</sup> the most important task in the study of the biological action of pesticides the development of the theory of predicting the pathology which may be caused by them, and the development of criteria of their potential and real danger. For this it is necessary to correlate<sup>the,</sup> data obtained in experiments with laboratory animals in comparatively short-term studies with the results of long-term observations during the entire life of the animal, as well as during the life of several generations. Of great importance is the comparison of the results of experimental and toxicological examinations with the data of hygienic and social-hygienic studies.

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METABOLISM AND PERSISTENCE OF PESTICIDES AND  
OTHER XENOBIOTIC CHEMICALS IN FISH

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Although studies in the early 1960's had indicated that fish do not metabolize drugs or foreign compounds to any extent, several investigators have demonstrated the presence of microsomal mixed function oxidases and conjugating enzymes in livers from several species of fish (1-3). The results of these investigations have indicated that many species are able to oxidize, dealkylate, reduce and conjugate foreign chemicals in vitro.

Based on these studies, the level of hepatic microsomal enzymes in many species of fish appear to be lower than that observed in mammals, but quantitative in vivo studies to substantiate this point have yet to appear. Even though biotransformation products can be formed enzymatically using fish liver preparations in vitro, it is difficult to predict from an in vitro study which, if any, such products will be formed during in vivo exposures. In a study involving the biotransformation of the lampricide 3-trifluoromethyl-4-nitrophenol (TFM) in rainbow trout, the formation of 3-trifluoromethyl-4-aminophenol and N-acetyl-3-trifluoromethyl-4-aminophenol was demonstrated using liver preparations in vitro (4). However, the only detectable metabolite formed in vivo during exposure to TFM was 3-trifluoromethyl-4-nitrophenol glucuronide which was excreted to a large extent in bile (5). The disposition of two other phenolic compounds (Bayer 73) and pentachlorophenol (PCP), have been studied in rainbow trout, and the major metabolite of both of these compounds appears to be the glucuronide conjugate, although conjugation of pentachlorophenol with sulfate has been reported in other species (6,7).

Studies of the fate of 1-naphthyl-N-methyl carbamate (Carbaryl) in rainbow trout have indicated that a major pathway of metabolism involves hydrolysis to 1-naphthol and conjugation of naphthol with glucuronic acid (8). Esters of the herbicide 2,4D undergo hydrolysis to the free acid in several species of fish (9,10).

Since enhanced excretion appears to be the consequence of conjugation of compounds possessing functional groups such as OH, NH<sub>2</sub> and COOH, with glucuronic acid, of great interest relevant to residue persistence is the oxidation of more non-polar compounds which do not have these groups such as

the polycyclic aromatic hydrocarbons found in crude oils and the polychlorinated biphenyls (PCB's). Naphthalene and 3,4 benzopyrene have been shown to be oxidized to more polar compounds by several species of marine fish, and these metabolites appear to be excreted in urine and bile (11). The polychlorinated biphenyls are highly persistent contaminants and residues of these compounds in fish have presented a major problem. Most studies have indicated very low rates of metabolism of the PCB's in fish and residue persistence is measured in terms of months or years (12,13).

Laboratory studies concerning biotransformation and persistence of xenobiotics in fish present some major obstacles when compared to mammalian investigations, and techniques which are directly relevant to the natural environment have been slow in development. Even relatively simple in vitro studies using liver preparations must be approached with an appreciation of the differences in optimal assay temperature (2) which exists among different species of fish as opposed to mammals.

Realizing that the tasks of evaluating a multitude of chemicals in many species of fish would be an enormous undertaking, attempts have been made to develop predictive methods for certain chemicals which have a high bioaccumulation and persistence potential. By measuring the rate constants for uptake and elimination in a constant flow exposure system, a theoretical bioconcentration factor can be calculated (14). This factor has been shown to be directly related to the partition coefficients of the compounds studied, and in a limited series, the calculated and experimental values appear to agree quite well (14).

Besides serving to clarify the relationship of biotransformation to the pharmacology and persistence of foreign chemicals in fish, information gleaned from these studies has some immediate practical applications. In many monitoring programs, analytical procedures are designed to determine residues of only the particular chemical under investigation and not its metabolites. In some instances this can be quite misleading. Muscle sampled from pinfish which were exposed to malathion for 24 hours contained little or no malathion but did have considerable concentrations of the monocarboxylic acid metabolite of malathion (15). Similar findings have been reported for esters of 2,4D (9). Even though the original chemicals were not detectable, the presence of metabolites revealed that the fish were exposed to the parent compounds, and this information in itself may be one of the more important considerations.

A possible application of studies concerning the biotransformation and biliary excretion of a number of xenobiotic chemicals is the use of fish bile sampling as an aid in monitoring for certain chemicals (16). In this study it was shown that many of the more water soluble compounds which do not have a high bioconcentration potential in tissues such as muscle are excreted in a highly concentrated form in bile. Sampling of bile from caged or wild fish in suspect areas may provide a convenient means of enhancing monitoring programs.



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## Pesticide Movement in the Organism of Farm Animals

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1. Pesticides may enter the organism of farm animals in feeds, water, air or through the skin when treating the animals to protect them against ectoparasites. However, only oral and cutaneous pathways are of practical importance.

2. Further fate of pesticides depends on the properties of chemicals, ways of their entering the organism, and animal species. Persistent organochlorine pesticides (DDT, HCCH, aldrin, heptachlorine, etc.) are resistant to the alimentary canal microorganisms and ferments, have poor water solubility and, therefore, slow excretion from the organism in urine, and, being lipoidophilic, may accumulate in adipose tissue. Organophosphorus and carbamate insecticides, herbicides—derivatives of phenoxy-acetic acid, series of triazines, urea, and many other pesticides are mostly decomposed by the alimentary canal microbes and ferments of the organism when entering through mouth. Polarity of these compounds is considerably higher than that of organochlorine pesticides and, therefore, they may be better excreted through urinary tract. In this connection, degree of material cumulation of organophosphorus and other

similar pesticides in the organism of farm animals, their excretion in milk and eggs when entering internally are hundred times lower than that of organochlorine compounds similar to DDT. Thus, if the coefficient of material cumulation "feed-fat" of various species of animals ranges from 5 to 20 for DDT, and from 0.5 to 1 for gamma-isomer HCCH, it is less than 0.01 for one of the most stable organophosphorus insecticides - trichlorometaphos-3. The level of excretion in milk for DDT and HCCH when entering internally is 5-10% of the residual amount in feed and it is 100-200 times lower for trichlorometaphos. Residues of organophosphorus and carbamate insecticides, herbicides, and fungicides, with the exception of mercuric compounds, in feeds for farm animals are of insignificant practical importance and are not able to exert a negative influence on the sanitary quality of animal production. Contamination of milk, meat, and eggs through feeds may mainly occur at the expense of organochlorine insecticides, heavy metals, PCB, arsenic, and other stable chemicals. This is confirmed by the results of numerous investigations of the animal production samples carried out in the Soviet Union, the United States, and other countries.

3. For ruminants (cattle and small cattle), decomposition of pesticides entering through mouth may mainly occur at the expense of the paunch microorganisms, whereas for poultry, the liver ferments play a decisive role. This is confirmed by the difference in the pathways of the p,p'-DDT metabolism. For ruminants, p,p'-DDT mainly metabolizes to p,p'-DDD. This pathway is possible un-

der the influence of anaerobes only. For poultry, most of the p,p'-DDT converts to p,p'-DDE that is characteristic for the fermental breakdown of this compound.

4. Penetration of nonpersistent pesticides in water is much more hazardous from the toxicological and sanitary point of view. For ruminants, toxicants together with water enter directly abomasum avoiding paunch, then small intestines and blood. In this case, hydrolyzing action of the paunch microbes is eliminated. Therefore, different physiological effect and residual content level in tissues and milk are observed when applying pesticides in feed and water at the same doses.

5. Somewhat different regularities were found in the pesticide behavior in the organism of farm animals under the external application. Well known are the long-term retention of DDT, HCCH, chlorinated terpenes, and other persistent pesticides in the organism of animals and their excretion in milk and eggs when spraying cattle and poultry. Therefore, organochlorine insecticides, with the exception of HCCH, are not used for the treatment of farm animals in the Soviet Union. Organophosphorus compounds are mainly used for this purpose. However, many lipoidophyllic organophosphorus compounds may be conserved in adipous tissue from 7 to 75 days under cutaneous application depending on the sort of pesticide, type of treatment, and species of animal. Most of the pesticides of this group are excreted in milk and eggs in larger quantities than when entering through mouth at the same doses. This appears to be accounted for by the fact that organophosphorus compounds may easily



penetrate in blood through undamaged skin and are not subjected to destructive action of the alimentary canal microbes, as it occurs when chemicals enter through mouth. In this connection, the necessity arises to investigate behavior in the organism of any pesticide which is recommended for the external treatment of animals to establish regulations for its use.

6. Organochlorine insecticides are mainly concentrated in the fat of animals as well as nonpolar organophosphorus compounds. Their content in other tissues is considerably lower. Degree of pesticide accumulation in fat and duration of their retention in tissues are inversely proportional to their polarity. Thus, 5 days after a single injection into sheep of diazinon (O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidyl)thiophosphate), phthalophos (imidane), trichlorometaphos-3, gamma-isomer HCCH, and pp'-DDT at the dose of 20 mgr per kg of weight, the residual level was: 0.4; 1.40; 1.60; 4.08, and 18.8 mg/kg - in fat and 0.01; 0.45; 0.40; 0.78, and 0.56 mgr/kg - in muscles, respectively. Therefore, the content of residual DDT in fat was higher than that in muscles by a factor of 33, HCCH - 5.3, trichlorometaphos-3 - 4, phthalophos - 3.1, and diazinon - 4. This data also shows that there is no substantial difference in residual contents of organophosphorus insecticides (phthalophos and trichlorometaphos-3) and organochlorine compounds (HCCH and DDT) in muscular tissue of sheep.

## MATHEMATICAL MODELING OF PESTICIDES IN THE ENVIRONMENT

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Several modeling and systems analysis techniques are particularly applicable to the problems presented by pesticide chemicals.

Component modeling of the processes affecting pesticides is well developed by comparison with our ability to coordinate these components in a model of a whole environmental system. Current modeling of pesticides treats their distribution as a transport phenomenon where the pesticide is associated with air, water, or soil/sediment movement. Specific process components are coupled to the transport model where they relate directly to the degradation, transformation, or transport-media exchange of the pesticide. The chronic, long-term effects and consequent ecosystem responses that are not represented in these models are now recognized to be as important as the short-term acute effects.

Total ecosystem models can be developed for pesticides; however, the data required to support realistic simulations in models of this resolution are prohibitive for a large number of pesticides. Linear approximations of total ecosystem models, which represent all processes as pseudo first-order processes, can be supported with considerably reduced data requirements and provide a format for sensitivity and worst case analyses.

The problems of identification of indirect environmental effects and evaluation of complex system interactions associated with pesticides can only be resolved through co-evolution of laboratory, field, and modeling approaches to these problems. The application of ecosystems theory, examining all the aspects of stress, stability, energy fluxes, nutrient cycles, carbon metabolism, and trophic structure in environmental systems, is emerging as one of the modern approaches to the complex problems of chemical pollutants. Although ecosystem models and analysis allow for evaluation of complex system interactions and for quantification of indirect environmental effects, their data requirements are prohibitive for application to most pesticides.

The developing theory of hierarchial models with nested levels of control and interactions among subsystems has a potential application to the pesticide problem. In applications of hierarchial modeling to pesticides in the environment, subsystems of a hierarchial, ecological model that are affected

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by the pesticide may behave without hierarchical constraint and the behavior of constrained subsystems may be observed as indirect responses to the pesticide in the context of higher level control and interaction. One of the problems associated with this application of hierarchical modeling theory is that environmental systems have a "closed causal structure."

Influence analysis provides quantitative measures of the organization of system structure and may allow a complex ecosystem model to be reduced to a minimal subset of aggregated components and condensed interactions such that the behavior of the complex model is qualitatively preserved. If the reduced model can be related to the constituents of a laboratory microcosm, then a link between laboratory experiment and whole system behavior may be established.

Research needs to be directed toward mathematical modeling that allows translation of laboratory measurements of pesticide effects on growth, physiology, and environmental interaction to field conditions. Thus, models need to be developed that estimate whole system behavior based upon data representing a limited set of component interactions. Hierarchical models with constrained subsystems and homomorphic structures derived from influence analysis may accomplish these goals in the near future.

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# QUALITY ANALYSIS AND NUMERICAL EXPERIMENT IN ANALYZING THE EFFECT OF THE ANTHROPOGENIC POLLUTION OF THE BIOTA

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I. Successful application of the mathematical modelling in various fields of science, e.g. physics, chemistry, meteorology, etc., revives hope in the efficiency of this method of research when used for tackling the analyzing of the effect of anthropogenic pollution on the biota. The analysis of the first results obtained in this way seems hopeful in regard of the promising aspects of the method if it is employed for solving the environment protection tasks, particularly, the multiparameter ones, as well as in studying the reaction to the exterior disturbance of the systems with the extremely complicated inner dynamics. Consequently, a necessity arises to intensify the further research devoted to the mathematical formulation of the environment protection problems and the progressive improvement of the methods of the mathematical modelling of these problems and their solution. However, it is worth mentioning here that in parallel with some specific difficulties inherent in these problems, the difficulties of a different nature have been revealed in the first publications on the question. These latter are mainly due to the overliberal approach to the solution of the tasks or with



a noncritical transfer of the knowledge acquired in other fields of science to the environment protection problem. In the first case, an unnecessarily voluminous experimental material undergoes mathematical processing which, as a rule, requires the involvement of the powerful modern computing devices without a serious preliminary analysis. That often leads to getting rather trivial results at the expense of much time and labour. In the second case, the mathematical models are developed on the basis of the differential equations in partial derivatives (the equations of convective diffusion, Shroedinger's equation, etc.) without sufficient grounds for using these types of equations to describe the processes under study.

2. The author is of the opinion that the following two ways look most promising for the analysis of the anthropogenic pollution effect on the biota with the help of the mathematical modelling:

- the quality analysis of the mathematical correlation formulated on the basis of the general quality reasoning concerning possible interrelation between various phenomena;

- the quantitative formulation of the mathematical correlation on the basis of the analysis of the experimental material and the general laws of science; carrying out of the numerical experiments with the help of this correlation.

The efficiency of the first way can be illustrated by Voltairre's model generalized by A.M. Kolmogorov and describing the inner dynamics in the "predator-prey" system with the stable fluctuations. The author has in this way analyzed the reaction of the biocenosis consisting of a single independent biological population to the

exterior disturbance. One of the essential results obtained has been represented in the established opportunity for the ecoresonance to appear in case of the combined exterior disturbances connected for instance with the anthropogenic pollution, and capable of causing some dramatic changes in the evolution of the biocenoses. The actual appearance of the ecoresonance in one or another biocenosis under the given conditions can be checked only through the numerical experiments.

The advantages of the second course can be substantiated by the Soviet and foreign publications of various tasks' solutions in the field of the environment protection.

# BASIC MATHEMATICAL MODELS OF TOXICANT TRANSPORT THROUGH THE SOIL PROFILE

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## I. Basic models

The general theory of sorption dynamics and chromatography [1,2] should be used for the theoretical description of toxicant transport through the soil profile. Specific feature of <sup>(in particular, pesticide)</sup> toxicant transport through the soil profile as compared with the ordinary sorption dynamics in a chromatographic column is the fact that apart from filtering transport and dynamic sorption, toxicant transport is accompanied by the processes of chemical and microbiological decomposition and transformation of pesticides. Moreover, in the soils with plants present a portion of a toxicant is absorbed and removed by plants. All these features may naturally complicate the quantitative description of dynamics of pesticide distribution through the soil profile. It is necessary to choose an inductive method to solve this problem (that is from the simple to the complex), first developing the simplest models and then gradually making them more complex. Let us work out basic sets of differential equations which may describe toxicant transport through the soil profile.

(I). The simplest model should provide for two physical processes: filtering toxicant transport in the flow of soil solution (under rain-fall and irrigation) and its dynamic sorption (toxicant sorption under the conditions of mobile liquid phase filtration). These processes may be described by a set of equations of material balance

$$\frac{\partial n}{\partial t} + u \frac{\partial n}{\partial x} + \frac{\partial N}{\partial t} = D * \frac{\partial^2 n}{\partial x^2} \quad (1)$$

and of sorption kinetics

$$\frac{\partial N}{\partial t} = f(n, N) \quad (2)$$

With a very slow filtration, it is possible to substitute the sorption isotherm equation

$$N = f(N) \quad (3)$$

for the sorption kinetics equation assuming an approximately equilibrium sorption process.

Solutions of the sets of equations (I-2) or (I-3) are given in many publications on the theory of sorption dynamics and chromatography (for example, [1,2]).

(2). In the absence of sorption, pesticide transport may be described with the filtering transport equation considering a longitudinal quasi-diffusion:

$$\frac{\partial n}{\partial t} + u \frac{\partial n}{\partial x} = D * \frac{\partial^2 n}{\partial x^2} \quad (4)$$

(3). When sorption is absent, but there exist a process of pesticide transformation (in particular, decomposition), it is necessary



to take into account the material loss by transformation:

$$\frac{\partial n}{\partial t} + u \frac{\partial n}{\partial x} = D^* \frac{\partial^2 n}{\partial x^2} + \chi(n) \quad (5)$$

where  $\chi(n)$  is the function of pesticide transformation kinetics.

(4). Finally, in the presence of sorption and pesticide transformation, a set of equations in general form will be:

$$\frac{\partial n}{\partial t} + u \frac{\partial n}{\partial x} + \frac{\partial N}{\partial t} = D^* \frac{\partial^2 n}{\partial x^2} + \chi(n) \quad (6)$$

$$\frac{\partial N}{\partial t} = f(n, N) \quad (7)$$

Correspondingly chosen initial and boundary conditions should be imposed on these sets of equations. These conditions predetermine various regimes of pesticide transport through the soil profile. By analogy with chromatography, it is possible to define three major regimes: frontal, elutive and displative [1,2]. Frontal regime occurs under continuous application of pesticide solution through the soil surface (for example, under irrigation). Elutive regime is at first an application of a portion of pesticide solution into the soil and then the soil washing with water. Displative regime is an application of a portion of pesticide solution into the soil and then the soil washing with a solution containing a substance which desorbs pesticide.

To study the processes of pesticide transport through the soil profile it is necessary to combine two methodological approaches: mathematical and physical experimentations.

Mathematical experimentation means compiling the specific sets of transport dynamics equations, solving them under given conditions

and working out functions of pesticide distribution through the soil profile.

Physical experimentation provides for carrying out physical experiments to study dynamics of pesticide distribution through the soil profile under given specific experimental conditions. Physical experiments will yield certain parameters which may be used for mathematical experimentation - simulation.

## 2. Asymptotic solution of the sorption dynamics problem using the kinetic parameter of time lag

An approximated sorption kinetics equation derived by the method of lagging coordinates using the parameter of time lag ( $\tau \ll t$ ) makes it possible to take into account a simultaneous influence of various factors on sorption kinetics disregarding specific mechanisms of the process. Here the lag constant  $\tau$  is considered to be determined experimentally [3].

A set of sorption dynamics and kinetics equations with the initial and boundary conditions takes the form:

$$\frac{\partial n}{\partial t} + u \frac{\partial n}{\partial x} + \frac{\partial N}{\partial t} = D^* \frac{\partial^2 n}{\partial x^2} \quad (8)$$

$$N(x, t) = f[n(x, t - \tau)] \approx f(n) - \tau \left( \frac{df}{dn} \right)^2 \frac{\partial n}{\partial t} \quad (9)$$

$$N(x, 0) = n(x, 0) = 0, \quad N(\infty, 0) = n(\infty, 0) = 0 \quad (10)$$

$$N(0, t) = N_0, \quad n(0, t) = n_0 \quad (11)$$

In a case of convex isotherm the stationary front of dynamic sorption is known to be formed in the column. Changing to the mobile coordinate system  $\xi = x - vt$ , where  $v$  is the velocity of the stationary front movement, it is possible to integrate the set of equations (8)-(9) and to transform it as follows:

$$\frac{dn}{d\xi} = \frac{n - hf(n)}{h\tilde{\epsilon}v\left(\frac{df}{dn}\right)^2 + \frac{D^*h}{v}}, \quad h = n_0/N_0 \quad (I2)$$

Let us introduce the relative concentrations  $\varphi = n/n_0$  and  $\vartheta = N/N_0$  and consider the Langmuir isotherm of sorption:

$$\vartheta = \frac{a\varphi}{1+b\varphi} \quad (I3)$$

where  $a - b = 1$ .

After algebraic transformations we may obtain the following expression:

$$\xi = \frac{\tilde{\epsilon}va^2}{h} \int \frac{d\varphi}{\varphi(1+b\varphi)^3(1+b\varphi-a)} + \frac{D^*h}{v} \int \frac{(1+b\varphi)d\varphi}{\varphi(1+b\varphi-a)} + C \quad (I4)$$

Now integrate the expression (I4) on the assumption that the isotherm is slightly curved, that is  $d\vartheta/d\varphi \approx \text{const.}$  (in a case of the Langmuir isotherm it is equivalent to the condition  $b \ll 1$ ) and determine the integration constant  $C$  [1,2]. Then we may obtain the following expression:

$$\xi = \frac{\tilde{\epsilon}v}{hb} \ln \frac{1-\varphi}{\varphi} + \frac{D^*h}{vb} \ln \frac{1-\varphi}{\varphi} = \frac{v}{bh} \tilde{\epsilon}' \ln \frac{1-\varphi}{\varphi} \quad (I5)$$

where

$$\tilde{\epsilon}' = \tilde{\epsilon} + \frac{D^*h^2}{v^2} \quad (I6)$$

Since from the solution of the set of equations (8)-(9) it follows that  $v = u \frac{h}{1+h}$ , the expression (15) may be finally written as follows:

$$x = u \frac{h}{1+h} \left( t + \frac{\tau'}{b} \ln \frac{1-\varphi}{\varphi} \right) \quad (17)$$

The expression (17) agrees with the result obtained in work [4] for the Langmuir isotherm and the diffusion kinetics equation  $\frac{\partial \varphi}{\partial t} = \beta h (\varphi - \varphi')$  where  $\beta$  is the sorption kinetics constant. In comparing it is seen that  $\beta = 1/\tau'$ . The introduced parameter additively allows for kinetic and longitudinal effects.

### 3. Equilibrium sorption dynamics at a variable velocity of the mobile phase

In some cases one has to study the process of toxicant sorption dynamics at a variable velocity of the mobile phase:  $u = f(t)$ . Let us consider the following initial set of equations for equilibrium sorption dynamics at a variable flow velocity:

$$\frac{\partial N}{\partial t} + \frac{\partial n}{\partial t} + u(t) \frac{\partial n}{\partial x} = 0 \quad (18)$$

$$N = f(n) \quad (19)$$

Using the change  $\partial \tau / \partial t = u(t) / [1 + f'(n)]$ , we may obtain the following expression from (18) and (19):

$$\frac{\partial n}{\partial \tau} + \frac{\partial n}{\partial x} = 0 \quad (20)$$

Now give the following initial conditions:  $t = 0 (\tau = 0), n = n_0 \varphi(x)$



where  $n_0$  is some characteristic concentration and  $\varphi(x)$  is the continuous function of initial material distribution.

The method of characteristics (initial value problem) for the expression (20) leads to the following formula:

$$n/n_0 = \varphi(x - \tau) = \varphi(\xi) \quad (21)$$

$$\text{where } \tau = \int_0^t u(t) dt / [1 + f'(n)] \quad (22)$$

Since  $\varphi(\xi)$  is the arbitrary function, it is possible to choose the unit function  $\ell(\xi) = \ell(x - \tau)$  as a solution. Then the solution to the equation (20) will also be the following function:

$$n/n_0 = 1 - \ell(\xi) + \varphi(\xi) \quad (23)$$

The solutions (21) and (23) satisfy the initial condition (20) and boundary conditions:

$$t > 0 (\tau > 0), x = 0, n = n_0 \quad (24)$$

$$t > 0 (\tau > 0), x = 0, n = 0 \quad (25)$$

The condition (24) is the frontal sorption dynamics and the condition (25) is the elutive sorption dynamics. The solutions (21) and (23) may also be obtained by the method of operational calculus. In this case the Laplace transformation must be performed first with respect to  $x$  and then with respect to  $t$ . A limitation of this method is that the validity of the solutions is only proved for the linear sorption isotherm.

From the solutions (21) and (23) we may obtain a generalized expression for Wicke law [5]:

$$\frac{dx}{dt} = v_n = \frac{d\tau}{dt} = \frac{u(t)}{1+f'(n)} \quad (26)$$

The solutions obtained are general, and the solutions of equilibrium sorption dynamics at  $u = \text{const.}$  are the special case of the obtained ones.

#### Designations

$n$  is the linear sorbate concentration in solution in the soil pores;

$N$  is the linear sorbate concentration in sorbed state;

$n_0$  is the initial and equilibrium concentrations of sorbate in solution;

$N_0$  is the equilibrium concentration of sorbate in sorbent which corresponds to the concentration  $n_0$ ;

$x$  is the distance from the soil surface level;

$t$  is the time of the process;

$D^*$  is the quasi-diffusion coefficient of longitudinal sorbate transport additively accounting all the factors of non-filtering longitudinal transport: molecular diffusion, hydrodynamic statistical non-uniformity of the mobile phase flow;

$\tau$  is the characteristic time lag formally accounting sorption kinetics.

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## MATHEMATICAL MODELING AND CONTROL AS A RADICAL WAY OF THE ENVIRONMENTAL PROTECTION FROM PESTICIDE CONTAMINATION

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The biospheric protection from pesticide contamination aimed at safeguarding the "healthy biosphere" is based on the complex of stages including prediction of the substance behavior and control over this process, check of the control accuracy, and introduction of the prediction and control corrections. L. I. Medved' (1971) points out that when considering the pesticides purposely dispersed in the environment, emphasis should be placed on the prediction stage. At the stage of preventive supervision it is necessary to work out regulations and standards as well as to test the conditions of pesticide application which provide the environmental protection.

Thus, preventive measures against contamination of the human habitation environment should be considered as a problem of control over the pesticide-environment system including all stages of the pesticide route:

1. Dissipation in the environment.
2. Distribution on the objects (plants, soil, water).



3. Behavior in each medium.
4. Migration between the media.
5. Total disappearance from the biosphere.

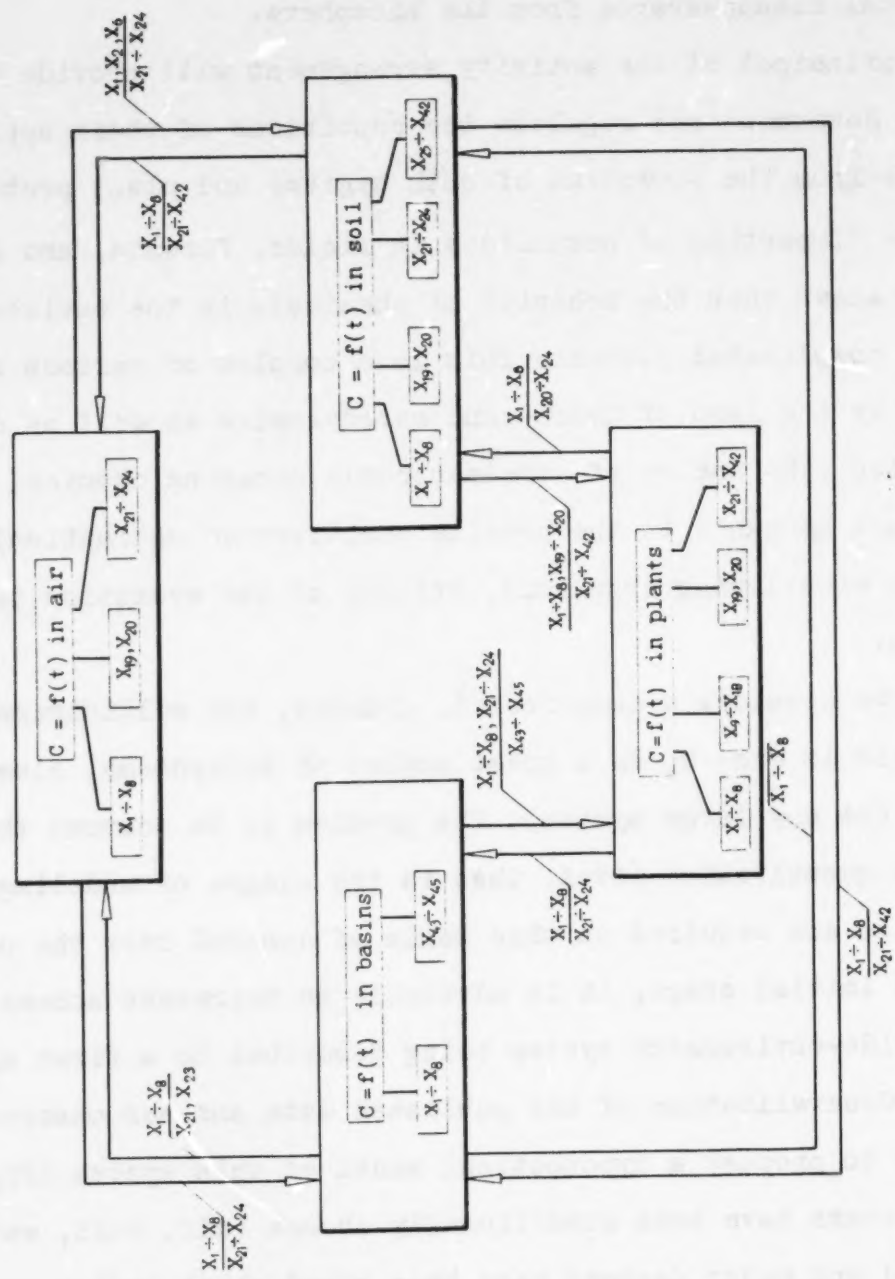
This principal of the activity arrangement will provide opportunities to determine and regulate the conditions of their application acceptable from the viewpoint of both hygiene and plant protection before the dispersion of pesticides in fields, forests, and gardens.

It is known that the behavior of chemicals in the environment is a very complicated process. This is a complex of various changes described by the laws of hydro- and aerodynamics as well as chemical kinetics (the number of simultaneously occurring chemical reactions is not amenable to the precise quantitative estimation), interactions with living organisms, effects of the evolution factors, and others.

Thus, we consider a complicated, dynamic, and multidimensional system which is made up of a great number of subsystems, elements, and bonds (as any large system). The problem is to control this system at the quantitative level, that is the stages of modeling-prediction also are required on this basis of control over the process.

As the initial stage, it is advisable to represent schematically the pesticide-environment system being described to a first approximation. Generalization of the published data and our observations enabled us to propose a hypothetical model of this system (Figure I). Four subsystems have been conditionally chosen (air, soil, water, and plants) and major factors have been named which define concentration as a function of time within each block and between them.

Fig. 1



To Figure I:

- X<sub>1</sub> is the pesticide molecular weight;  
 X<sub>2</sub> is the temperature of pesticide melting (boiling);  
 X<sub>3</sub> is the fat solubility;  
 X<sub>4</sub> is the water solubility;  
 X<sub>5</sub> is the pesticide persistence at pH of 5-8;  
 X<sub>6</sub> is the pesticide volatility;  
 X<sub>7</sub> is the pesticide persistence at pH of 5;  
 X<sub>8</sub> is the pesticide persistence at pH of 8;  
 X<sub>9</sub> is the plant pH;  
 X<sub>10</sub> is the water content of plants;  
 X<sub>11</sub> is the total acidity;  
 X<sub>12</sub> is the nitrous substance amount;  
 X<sub>13</sub> is the fat amount in plants;  
 X<sub>14</sub> is the cellulose amount;  
 X<sub>15</sub> is the ashes content;  
 X<sub>16</sub> is the pectinic substance amount;  
 X<sub>17</sub> is the content of proteins;  
 X<sub>18</sub> is the total amount of sugars;  
 X<sub>19</sub> is the frequency of treatments;  
 X<sub>20</sub> is the rate of pesticide application on treatment;  
 X<sub>21</sub> is the average air temperature;  
 X<sub>22</sub> is the total precipitation;  
 X<sub>23</sub> is the relative air humidity;  
 X<sub>24</sub> is the velocity of air movement;  
 X<sub>25</sub> is the humus content in soil;  
 X<sub>26</sub> is the soil pH;  
 X<sub>27</sub> is the absorbing capacity;  
 X<sub>28</sub> is the soil moisture capacity;  
 X<sub>29</sub> is the soil density;  
 X<sub>30</sub> is the mechanical composition of soil;  
 X<sub>31</sub> is the total absorbed bases;  
 X<sub>32</sub> is the amount of phosphorus compounds;  
 X<sub>33</sub> is the nitrous substance content;  
 X<sub>34</sub> is the amount of fertilizers applied;  
 X<sub>35</sub> is the microorganisms;  
 X<sub>36</sub> is the species of nurse crop;  
 X<sub>37</sub> is the yielding capacity of nurse crop;  
 X<sub>38</sub> is the depth of root system bedding;  
 X<sub>39</sub> is the trade mark of the chemical which entered the soil;  
 X<sub>40</sub> is the way of chemical application;  
 X<sub>41</sub> is the average soil temperature;  
 X<sub>42</sub> is the soil moisture;  
 X<sub>43</sub> is the water pH;  
 X<sub>44</sub> is the amount of oxygen dissolved in water;  
 X<sub>45</sub> is the water temperature;  
 and others.

Questions arise concerning the process of pesticide interaction within each subsystem as well as changes of the effect with changing these or those input and internal variables and interactions between the adjacent media. The number of measurements necessary to describe these processes is incredibly great (the level and duration of pesticide content, meteorological parameters, biochemical and chemical reactions, etc.). It is impossible to take account of all these factors experimentally as a great number of variables and variants of interactions changes. Necessity is evident to use the methods of cybernetic modeling for description of the problems of this kind.

Let us consider this approach using as an example the pesticide-plant subsystem.

We have systematized and classified the data of world publications and our experimental investigations in dynamics of degradation of pesticides belonging to different chemical classes in various species of plants under the varying conditions of application. When generalizing this information, an attempt has been made to reveal the sequence of the pesticide-plant interaction mechanisms taking place and factors which determine them. There is little information on this problem.

It has been found that a number of biotic and abiotic factors are of substantial significance in the process of pesticide degradation and that the physical and chemical properties of compounds play a leading role in the outcome of the process of interaction with plant organism. Of great importance in the mechanism of pesti-



cide transformation are the factors of plants. So when applied on the plant, the stock of substance undergoes a number of quantitative and qualitative changes under the influence of the experimental conditions and properties of plant surface. Penetrating deep into plant tissue, pesticide may undergo various transformations in hydrophilous fractions and accumulate in lipophilous tissues. Formation of complex compounds with carbohydrates, amino acids, and other plant components may be one of the forms of substance transformation. There are various types of pesticide biotransformation: oxidation, hydroxylation, epoxidation, N-dealkylation, dehalo- and dehydrogenation, conjugation with sugars, etc. It is evident that plant enzymes have a dominant role in the processes of pesticide degradation and transformation.

However, the information available covers only individual small links in the chain (or chains) of numerous reactions of the pesticide-plant interaction.

It should be emphasized that since the process of this interaction occurs under the conditions of continuously varying numerous factors of the environment, these latter have a pronounced effect on the outcome of the process causing new numerous bonds and reactions.

The foregoing proves that it is very difficult to choose the type of mathematical description of the process being considered.

When describing complex systems, complete knowledge of the process is commonly absent. Then one may neglect the "unessential factors", random effects, influence of the conditions external to the

given system, and other uncertainties in the information and if it is still possible to gain a general idea of the behavior of chemical and a role of the essential factors, the classic apparatus of differential equations can be used. However, such information is not available for the subsystem being considered in terms of the problem set.

It is evident that advisable is the use of the models on the "black box" principle. Probability statistical approach makes it possible to be satisfied with the information on the actual course of the process digressing from the essence of physical and chemical, and chemical and biological reactions.

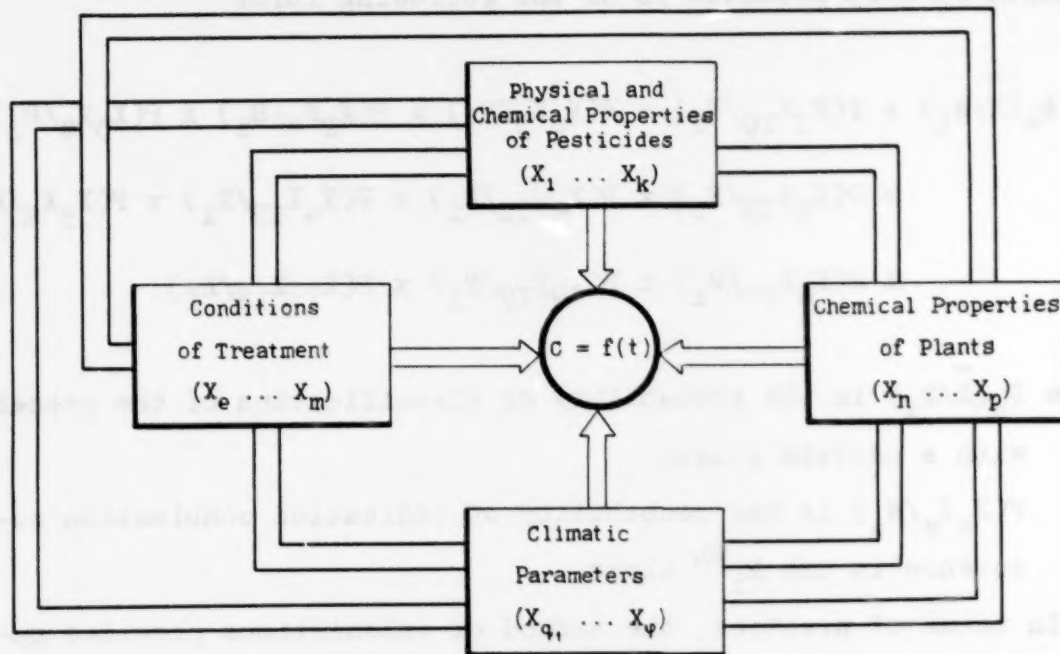
In the last few years the theory of image identification has been used to predict multidimensional process with the information of this kind available. To synthesize the model we have used one of the methods of heuristic self-organization, namely the method of group analysis of arguments (Ivakhnenko, A.G., 1971).

The information accumulated contains the data on 90 processes of pesticide degradation in fruit and vegetable (except roots and tuber-plants). The data have been analyzed which characterize kinetics of 15 pesticides belonging to different chemical classes under various conditions of their application. 22 indications, both direct and indirect, were taken into account and quantitatively evaluated (we used direct measurements and the method of expert estimates). Analysis of these data showed that four groups of factors affect the rate of pesticide degradation (Figure 2):

I. Physical and chemical properties of pesticides (molecular

- weight, melting temperature, fat solubility, water solubility, persistence at different pH values, volatility).
2. Treatment conditions (number of treatments, rates of pesticide application).
  3. Climatic parameters of the environment (average air temperature over the period from the beginning of treatments to the end of investigations, total precipitation over the same period).
  4. Properties of plants.

Fig. 2



Determination of these latter turned out to be the most complicated. Taking into consideration that the problem is not clearly understood and the information available is scant, we assumed hypothetically that all components of the chemical composition of plants directly or indirectly participate in the process of pes-

ticide interaction with plants. In accordance with this, the following factors were considered: pH of the culture, water content of plant, total acidity, nitrous substances, fats, cellulose, pectinic substances, ashes, proteins in culture, total amount of sugar in plant.

Exponent has been used as an approximating function of dynamics of the process being studied. Classification has been performed with the time constant value.

The formula of identification of the pesticide conservation duration in crop products is of the following form:

$$P_a(\bar{X}/R_1) = P(X_I X_{IO}/R_1) \times P(X_2 X_3/R_1) \times P(X_2 X_4/R_1) \times P(X_3 X_4/R_1) \times \\ \times P(X_3 X_{I3}/R_1) \times P(X_4 X_{IO}/R_1) \times P(X_4 X_{I9}/R_1) \times P(X_5 X_6/R_1) \times \\ \times P(X_6 X_{2I}/R_1) \times P(X_9 X_{I7}/R_1) \times P(X_{I3} X_{I8}/R_1)$$

where  $P_a(\bar{X}/R_1)$  is the probability of classification of the process with a certain class;

$P(X_k X_e/R_1)$  is the probability of indication combination occurrence in the  $R_1^{th}$  class.

In terms of practice, the method of calculations provides opportunities to predict the level of residues and life duration of a given pesticide in various cultures at different climatic parameters and under different conditions of its application.

Verification has been made at the experimental plots in eight climatic and geographical zones of the Soviet Union (Estonia, Lat-



via, Lithuania, Byelorussia, Ukraine, Moldavia, Georgia, Armenia) to test the hypothesis validity and possibility to use the formula. The results of comparison between the calculated data and actual information obtained at the experimental plots in the above-mentioned zones of the country showed that the average accuracy of prediction was 70%.

Several examples are given in Tables I,2 and Figures 3,4.

Table I. Comparison of the actual and calculated data on the duration of conservation of several organophosphorus pesticides in apples and tangerines

| Pesticide  | : Duration of conservation |    |                             |    |                           |    |                             |    |                 |    |
|------------|----------------------------|----|-----------------------------|----|---------------------------|----|-----------------------------|----|-----------------|----|
|            | : Pozalon : (zolon) :      |    | : Phthalophos : (imidane) : |    | : Anthio : (formothion) : |    | : Carbophos : (malathion) : |    | : Phosphamide : |    |
| Culture    | : Act.:Calc. x)            |    | : Act.:Calc. :              |    | : Act.:Calc. :            |    | : Act.:Calc. :              |    | : Act.:Calc. :  |    |
|            | :                          | :  | :                           | :  | :                         | :  | :                           | :  | :               | :  |
| Apples     | 30                         | 35 | 20                          | 26 | 18                        | 25 | 18                          | 25 | 20              | 26 |
| Tangerines | 12                         | 21 | 12                          | 21 | 18                        | 25 | 17                          | 21 | 12              | 20 |

x) Upper limit of the calculated value.

These data were obtained by L. G. Adeishvili, 1975.

The stages mentioned - model synthesis and prediction are necessary to achieve the primary practical purpose - control over the pesticide-plant system with regard to the requirements of hy-

Table 2. Comparison of the actual data on the duration of conservation of several organophosphorus pesticides in cherries and sweet cherries

|                |    |                          |    |                     |    |              |    |             |    |         |   |       |   |      |   |       |   |      |   |       |
|----------------|----|--------------------------|----|---------------------|----|--------------|----|-------------|----|---------|---|-------|---|------|---|-------|---|------|---|-------|
| Pesticide      | :  | Cidial                   | :  | Carbophos           | :  | Metathion    | :  | Phosphamide | :  | Fozalon |   |       |   |      |   |       |   |      |   |       |
|                | :  | (papthion)               | :  | (malathion)         | :  | (byer 4183I) | :  |             | :  | (zolon) |   |       |   |      |   |       |   |      |   |       |
|                | :  | Duration of conservation |    |                     |    |              |    |             |    |         |   |       |   |      |   |       |   |      |   |       |
| Culture        | :  | Act.                     | :  | Calc. <sup>x)</sup> | :  | Act.         | :  | Calc.       | :  | Act.    | : | Calc. | : | Act. | : | Calc. | : | Act. | : | Calc. |
|                | :  | :                        | :  | :                   | :  | :            | :  | :           | :  | :       | : | :     | : | :    | : | :     | : | :    | : | :     |
|                | :  | :                        | :  | :                   | :  | :            | :  | :           | :  | :       | : | :     | : | :    | : | :     | : | :    | : | :     |
| Cherries       | 20 | 25                       | 16 | 16                  | 15 | 16           | 20 | 25          | 48 | 60      |   |       |   |      |   |       |   |      |   |       |
| Sweet cherries | 20 | 25                       | 15 | 16                  | 11 | 16           | 21 | 24          | 50 | 62      |   |       |   |      |   |       |   |      |   |       |

<sup>x)</sup> Upper limit of the calculated value

These data were obtained by E. K. Ordzhonikidze, 1975

Fig. 3

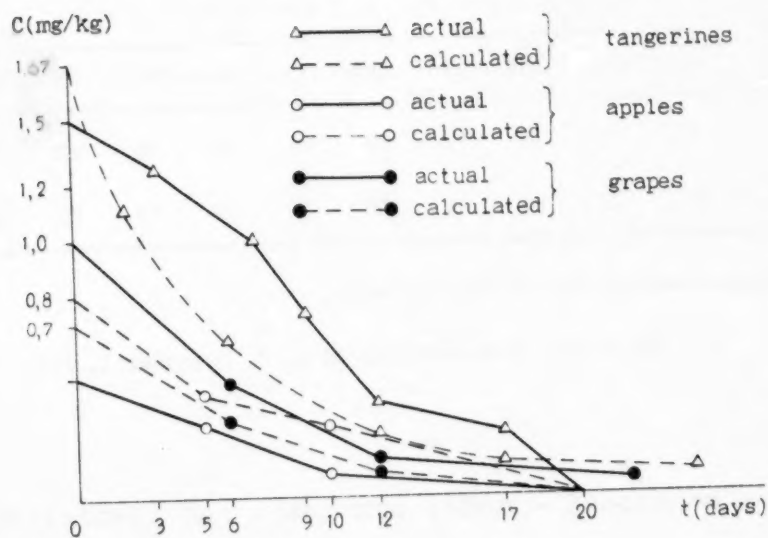
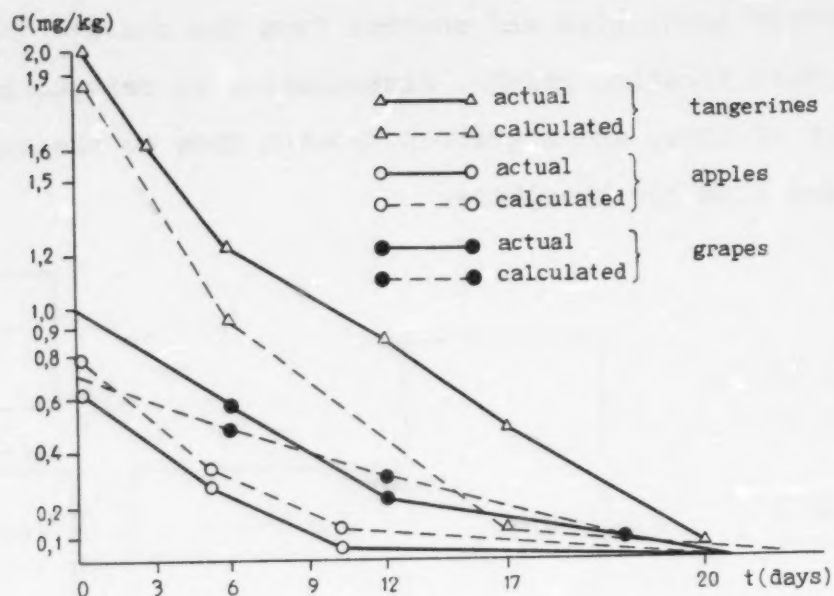


Fig. 4



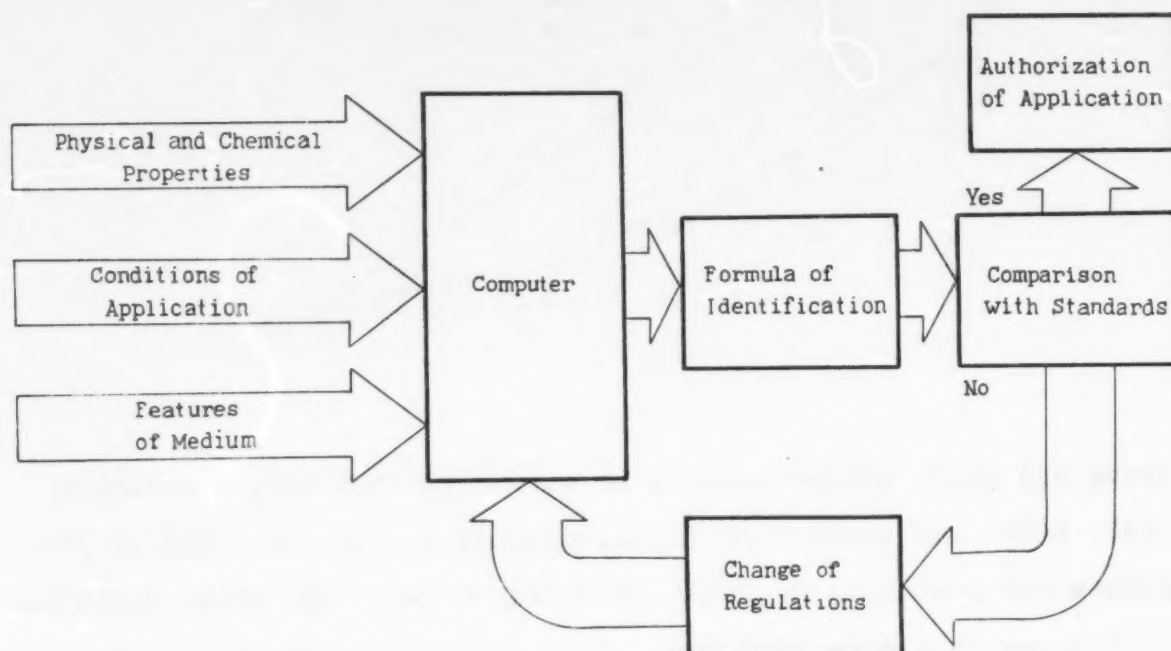
giene and plant protection. It is essential that when predicting time, site, and numbers of pests, calculation of the level of residues and pesticide degradation duration under the given specific conditions should be performed. This combined prediction will provide opportunities to choose the control decision approaching the optimal one.

On the basis of these data it is possible to perform sorting out of variants (pesticide assortment, species of culture, etc.). The general diagram of control over the process is shown in Figure 5 where computer symbolizes the predicting system which can be the prediction formula at the lowest level of organization and State predicting system - at the higher level.

Description of the individual environmental components as a large and complex system is the most important element of the pes-

ticide behavior prediction and control from the moment of pesticide dispersion when treating plants, distribution in various media, fate in each of them, and migration between them to the complete disappearance from the biosphere.

Fig. 5



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## MODELING OF PESTICIDE DEGRADATION IN PLANTS AND EVALUATION OF THEIR APPLICATION SYSTEMS

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Increasing efficiency of the preventive system of pesticide contamination of crop production is possible under the properly chosen conditions of pesticide application (rates of pesticide application, frequency of treatments, terms of carrying out treatments before harvesting) with regard to the persistence of these substances and properties of the medium. A possibility to choose an acceptable variant of the conditions mentioned should be created before carrying out treatments.

One of the ways to solve this problem is the use of the methods of modeling, prediction, and monitoring. The second step is presently made on the way of mathematical modeling of pesticide content dynamics in plants consisting in the development of an improved mathematical model (L. N. Ivanova, 1976). The first step on this way was the previously developed probability model covered rather comprehensively in several publications (A. G. Ivakhnenko, et al., 1972; E. I. Spynu, L. N. Ivanova, 1975; etc.).

The previously developed probability model provides a simplified calculation of pesticide level and duration of conservation in fruit and vegetables which is acceptable for practical use; however, this model has somewhat limited possibilities of predicting and monitoring the process of contamination. To develop this model the problem of statistical classification of the processes being studied by the level of pesticide content and duration of their conservation has been solved, that is the parameters mentioned have been divided into several classes. As a result, the prediction amounts to identifying the class into which the predicted quantity falls.

Natural was a desire to develop a more accurate model of pesticide disappearance from plants for the purpose of prediction. Some investigators believe that the most accurate models which more completely reveal the regularities of the phenomena being studied can be developed by means of the apparatus of differential equations. It has been this approach that has been applied along with the algorithm of differential identification.

It should be noted that in modeling pesticide degradation a great body of information on the cause and effect relationships was brought a priori. There is no doubt that in so complicated phenomenon as the process being studied these relationships were not clearly traced, the more so as the mechanism of its proceeding was not revealed equally and completely for the majority of pesticides. However, the information on possible mechanisms is contained in the experimental data and can be used for solving the

problem of prediction. Mathematical methods have been developed to handle incomplete and inaccurate information characterized by both direct and indirect indications. These methods provide prediction accuracy acceptable for practical use. We used one of them, namely the method of group analysis of arguments synthesized by A. G. Ivakhnenko (1971) in modeling the process of pesticide disappearance in plants. This method was used to solve other practical problems, such as calculation of hydrobiological parameters (J. Duffy and H. Franklin, 1973) and others.

The process of pesticide content reduction in the plants contaminated by them can be described by the following equation:

$$\frac{dC(\bar{X}, t)}{dt} = C(\bar{X}, t) \left[ K_1(\bar{X}) + K_2(\bar{X})C(t) + \dots + K_n(\bar{X})C(t)^n - I \right] \quad (1)$$

where  $K_1(\bar{X}), K_2(\bar{X}), \dots, K_n(\bar{X}) < 0$  are the negative constants of the rate of the process;

$\bar{X}$  is the vector characterizing the physical and chemical properties of pesticides, features of plants, conditions of treatments, and climatic parameters.

An acceptable accuracy is obtained with two members on the right side of the equation available. Direct integrating is possible providing

$$\frac{dK_1(\bar{X})}{dt} = \frac{dK_2(\bar{X})}{dt} = 0,$$

and each individual process is described by an equation of the form:

$$C(\bar{X}, t) = \frac{C_0(\hat{X}) \cdot e^{-K_I(\bar{X})t}}{1 + C_0(\hat{X}) \frac{K_2(\bar{X})}{K_I(\bar{X})} \cdot [1 - e^{-K_I(\bar{X})t}]} \quad (2)$$

where  $C(\bar{X}, t)$  is the current pesticide concentration;

$C_0(\hat{X})$  is the initial pesticide content in the vegetative object;

$K_I(\bar{X})$  and  $K_2(\bar{X})$  are the constants of the rate of the pesticide degradation process.

It is possible to restrict oneself to one member on the right side of equation (1) and approximate the contamination reduction process to exponent. The description obtained provides possibilities to determine the rate constants  $K_I(\bar{X})$  and  $K_2(\bar{X})$ , and the current concentration  $C(\bar{X}, t)$  from the values of vector  $\bar{X}$  known beforehand at the moment of time  $t$  which is of interest to us.

The process being studied is amenable to control, and the propositions worked out to fit the control systems are valid for it. According to R. Lee (1966), two problems are to be solved to analyze these control systems:

1. Direct problem - the description of dynamics of the object, or process being studied.

2. Inverse problem - the indication (finding) of parameters from the experimental data.

So we have made an attempt to solve both problems for the process of pesticide degradation, that is not only develop the description of an individual process but also identify its constants



and, using them, predict the output value  $C(\bar{X}, t)$ . This provides opportunities to control a given value by means of the properly chosen conditions of carrying out treatments.

Using the prediction formulas, it is possible to calculate the moment of time at which pesticide treatments of farm crops are to be carried out before harvesting, that is the so called waiting time ( $t_w$ ), with the values limiting food stuff contamination available (PRA - permissible residual amounts).  $t_w$  can be calculated with formula (3) assuming the first order kinetics to be dominant in the process of pesticide disappearance:

$$t_w = \frac{\ln \text{PRA} - \ln C_0(\hat{X})}{K_I(\bar{X})} \quad (3)$$

From the hygienic viewpoint, the relation between the predicted level of pesticide content in the object which is of interest to us, that is  $C(\bar{X}, t)$ , and the value of PRA can be used as a certain dimensionless index of safe application of a given chemical. Residues of several pesticides may be found in the yield by the moment  $t_w$  due to the wide-scale use of the systems of farm crop chemical protection with certain assortment of chemicals and sequence of their application. To evaluate food stuff contamination in this case it is necessary to introduce an index defining safety of these systems of plant protection. As one of these indices, the dimensionless quantity can be used which is calculated with the following formula:

$$Q(t_w) = \sum_{i=1}^n \frac{C_i(\bar{X}, t_w)}{K_1 \cdot PRA_1} \leq 1 \quad (4)$$

where  $Q(t_w)$  is the safety index of the system which is always less or equal to unity;

$K_1$  is the reserve coefficient which allows for possible newly revealed adverse effect of the pesticides being studied;

$C(\bar{X}, t_w)$  is the concentration of the  $i^{\text{th}}$  pesticide at the moment of harvesting.

Thus, the obtained mathematical models of pesticide degradation in plants provide opportunities to calculate an approximate level of pesticide contamination of fruit and vegetables and not only determine but also choose the acceptable regulations of pesticide application (waiting time). The formulas have been developed which make it possible to evaluate safety of the application of one pesticide as well as of a system of quite a number of chemicals.

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THE MODEL OF THE PESTICIDE CIRCULATION  
IN FERGANA VALLEY

(Koropalov V.M., Nazarov I.M.)

In this paper by an example of Fergana Valley a mathematical model is considered, which describes pesticides circulation in the intermountain valley with a limited release outside. We were interested in what aspects of the pesticide cycle are principal and what is the possibility to assess the permissible loading on the ecosystem. We tried to obtain adequate description of the pesticide circulation with the help of minimum number of parameters, which for rather reliable estimates could be obtained. In Fergana Valley DDT was used until 1970 when it was prohibited. /1,2,3/. Residual amount of DDT circulating in the ecosystem, allowed us to get experimentally a number of transfer parameters, a part of parameters being taken from literature. /7,8,9/. We consider pesticides transfer between the atmosphere, soil, water and vegetation. In Fergana Valley a rather high agricultural cultivation of the territory caused a wide development of erosion /4/. This, in its turn, favours soil particles polluted with pesticides to enter the atmosphere as a result of weathering. At the same time a high air temperature in this region favours pesticides evaporation from the soil surface and vegetation and then volatilizing with water vapours.



Life-time of gaseous and aerosol fractions of pesticides in the atmosphere differ significantly, so it seemed reasonable to consider aerosol and gaseous fractions of the pesticides in the atmosphere separately. Further, since pesticides are applied not over the whole area of the valley, all the soil in the model is divided into two parts: soil I - fields treated with pesticides; soil II - the residual area of the valley where pesticides were not applied. Due to this very reason we consider vegetation only on soil where pesticides are not applied directly. The differential equation set describing the circulation of pesticides between the ecosystem media, can be written as following

$$\frac{dC_1}{dt} = \frac{(1-f_1)f_2P}{m_1} + \frac{1}{m_1} \left( \frac{m_3C_3}{T_{31}} + \frac{m_4C_4}{T_{41}} \right) - \frac{C_1}{T_1}$$

$$\frac{dC_2}{dt} = \frac{(1-f_1)(1-f_2)P}{m_1} + \frac{1}{m_1} \left( \frac{m_3C_3}{T_{32}} + \frac{m_4C_4}{T_{42}} \right) - \frac{C_2}{T_2}$$

$$\frac{dC_3}{dt} = \frac{f_1P}{m_3} + \frac{1}{m_3} \left( \frac{m_1C_1}{T_{13}} + \frac{m_2C_2}{T_{23}} \right) - \frac{C_3}{T_3}$$

$$\frac{dC_4}{dt} = \frac{1}{m_4} \left( \frac{m_1C_1}{T_{14}} + \frac{m_2C_2}{T_{24}} + \frac{m_5C_5}{T_{54}} \right) - \frac{C_4}{T_4}$$

$$\frac{dC_5}{dt} = \frac{1}{m_5} \left( \frac{m_1C_1}{T_{15}} + \frac{m_2C_2}{T_{25}} + \frac{m_3C_3}{T_{35}} \right) - \frac{C_5}{T_5}$$

$$\frac{dC_6}{dt} = \frac{1}{m_6} \left( \frac{m_1C_1}{T_{16}} + \frac{m_2C_2}{T_{26}} + \frac{m_4C_4}{T_{46}} \right) - \frac{C_6}{T_6}$$

where  $C_1, C_2$  - pesticide concentration in the atmosphere, in aerosol and vapour phases, respectively .

$C_3, C_4$  - pesticide concentration in soil I and II.

$C_5$  - pesticide concentration in water.

$C_6$  - Pesticide concentration in vegetation.

$m_{1,2} = V$  - atmosphere volume of Fergana Valley.

$m_{3,4}$  - mass of the surface layer of soil I and II.

$m_5$  - water mass.

$m_6$  - vegetation mass.

$P$  - velocity of incoming pesticides into the valley.

$f_1$  - a fraction of pesticides falling-out directly on the fields during treatment.

$f_2(1-f_1)$  - a fraction of pesticides released into the atmosphere in the form of aerosols during field treatment.

$(1-f_2)(1-f_1)$  - a fraction of pesticides released into the atmosphere in the form of a vapour phase during field treatment.

$T_{ij}$  - retention time of pesticides in  $i$ -th medium determined by pesticides transfer from  $i$ -th medium into  $j$  ( $i \neq j$ )

$T_{ii}$  - retention time of pesticides in  $i$ -th medium, determined by direct decomposition in  $i$ -th medium.

$T_i$  - total retention time of pesticides in  $i$ -th medium.

$$\frac{1}{T_i} = \sum_j \frac{1}{T_{ij}}$$

Now let us consider and assess pesticide fluxes between various media of our ecosystem. Further all specific estimations of the pesticides fluxes will be performed for DDT which found the widest application.

Its displacement between different media is studied most completely compared with other pesticides / IO,II/. When developing the model, the amount of DDT released into the atmosphere at the moment of application and due to secondary application is supposed to be homogeneously mixed throughout the whole air volume of Fergana Valley and then fall-out uniformly over the whole area. The sedimentation velocity of DDT, connected with a coarse-dispersed aerosol according to our data is within  $(0.4-1.2) \cdot 10^{-2}$  m/sec. For the DDT vapour sedimentation from the atmosphere two estimates are known, namely,  $4 \cdot 10^{-4}$  cm/sec and  $5 \cdot 10^{-2}$  m/sec. In the first case the rate of DDT vapour deposition on glass was measured, in the second one - that on water surface /9/.

Usually, vapour and aerosol pesticides phase present in the atmosphere simultaneously. It is found, that often only about half of DDT in the atmosphere is in the vapour phase and in the atmosphere with increased aerosol content this part is still less /9/. To take into account the effect of meteorological parameters on the atmospheric transfer of DDT there was considered a two-layer atmospheric model of Fergana Valley. Vertical distribution of DDT in the atmosphere both for aerosols and vapours was described with the help of the equation:

$$C_{1,2}(z) = \begin{cases} C_{1,2}(0) \exp\left(-\frac{v_{1,2}}{K_1} z\right) & 0 \leq z \leq z^* \\ C_{1,2}(0) \exp\left[-\frac{v_{1,2}}{K_1} z^* - \frac{v_{1,2}}{K_2} (z - z^*)\right] & z^* \leq z \leq H \end{cases}$$

where  $K_1, K_2$  - coefficients of turbulent exchange in the lower and upper layer.

$v_{1,2}$  - sedimentation velocity of DDT vapour and aerosols, respectively .

$z^*, H$  - the altitude of the lower and upper layer of the atmosphere, respectively .

$C_{(0)}^{1,2}$  - surface air concentration of DDT vapour and aerosols, respectively.

With allowance for particularities of the air-mass exchange in Fergana Valley / 5 / DDT transfer beyond its limits can take place throughout the year only across the upper atmosphere boundary and periodically in case of Ursatjevsky wind. Though methods of pesticide income can be various, in principle they reach soil surface. Soil is like a reservoir for pesticides where they are either transferred into other media or decomposed. Quantitative assessments of pesticide flows due to uptake by plant root system, washout with surface run-offs, carrying away with dust, and volatilization were taken from papers / 6, 9, 12/. The systematic application of pesticides on areas the most part of which is a watershed, leads to a fact, that run-off of melted snow, rain and irrigating waters from agriculture fields becomes a source of water-bodies pollution. Waste waters from the irrigated territory of Fergana Valley are removed into continuous hollows and rivers. DDT decomposition in water was studied in paper / 6/. It was found that time of DDT decomposition in water changed within 112-139 days depending on pH. Since the river system has its output beyond the valley, part of pesticides will be carried away due to natural water exchange.

With a help of our model we tried to follow dynamics of DDT redistribution in Fergana Valley throughout a year. DDT concentration



in different media was calculated with a period of a month. Mean values of parameters used in the model are given in Table I. Some parameter values (showing DDT income into the system, valley airing,

Table I  
Mean Values of Model Parameters

|             |                                   |
|-------------|-----------------------------------|
| $m_1$       | $45 \cdot 10^3 \text{ km}^3$      |
| $m_2$       | $45 \cdot 10^3 \text{ km}^3$      |
| $m_3$       | $24 \cdot 10^8 \text{ t}$         |
| $m_4$       | $63.6 \cdot 10^8 \text{ t}$       |
| $m_5$       | $50 \cdot 10^8 \text{ t}$         |
| $m_6$       | $8 \cdot 10^6 \text{ t}$          |
| $f_1$       | 0.5                               |
| $f_2$       | 0.5                               |
| $f_3$       | 0                                 |
| $\bar{z}^*$ | 0.2 km                            |
| $H$         | 2 km                              |
| $K_1$       | $1 \text{ m}^2/\text{sec}$        |
| $K_2$       | $10 \text{ m}^2/\text{sec}$       |
| $v_2$       | $1 \cdot 10^{-2} \text{ m/sec}$   |
| $v_1$       | $1 \cdot 10^{-4} \text{ m/sec}$   |
| $K(3,1)$    | $1 \cdot 10^{-4} \text{ 1/month}$ |
| $K(3,2)$    | $2 \cdot 10^{-2} \text{ --}$      |
| $K(3,3)$    | $1.1 \cdot 10^{-1} \text{ --}$    |
| $K(3,5)$    | $2.5 \cdot 10^{-3} \text{ --}$    |
| $K(4,1)$    | $1.1 \cdot 10^{-4} \text{ --}$    |
| $K(4,2)$    | $2 \cdot 10^{-2} \text{ --}$      |
| $K(4,4)$    | $1.1 \cdot 10^{-1} \text{ --}$    |
| $K(4,6)$    | $1.7 \cdot 10^{-3} \text{ --}$    |
| $K(5,4)$    | $1 \cdot 10^{-1} \text{ --}$      |
| $K(5,5)$    | $1.1 \text{ --}$                  |

$$K(i,j) = \frac{1}{T_{ij}}$$

DDT evaporation from cultivated fields) change considerably throughout a year so they were taken as time functions. Thus rate of DDT incoming into the system was described with a function

$$P = \frac{P_1(1+f_3t)}{1+\left(\frac{t-6}{3}\right)^8} \quad 0 \leq t \leq 12$$

where  $P_1$  - amount of DDT entered the valley for a month during a period of maximum application,  $f_3$  - coefficient of increased DDT application. In this paper we give only calculations for a constant velocity of application of DDT (i.e.  $f_3 = 0$ ) at a rate of 10 kg/ha. The decrease of DDT concentration in the atmosphere when airing the valley, was as following

$$\frac{dC_{1,2}}{dt} = -C_{1,2} \frac{\cos^2\left(\frac{\pi t}{12}\right)}{T_{II}} \quad 0 \leq t \leq 12$$

where  $T_{II}$  = one day, i.e. valley airing for a period from June to December is supposed to increase from null to maximum possible. Results of some calculation versions are given in Fig. 1-2. The relation of vapour phase to aerosol one equal to 1:2 was assumed to remain constant in the atmosphere. Initial concentration in all media was supposed to be equal to zero. Redistribution of DDT between media was calculated for the first two years since the start of DDT application. The change of a mean atmospheric concentration of DDT associated with the aerosol for two states of the atmosphere is shown in Fig. 1. In <sup>the</sup> first case a good mixing in the atmosphere ( $K_1 = 10 \text{ m}^2/\text{sec}$  for the whole atmosphere of the valley) and airing are supposed. In the

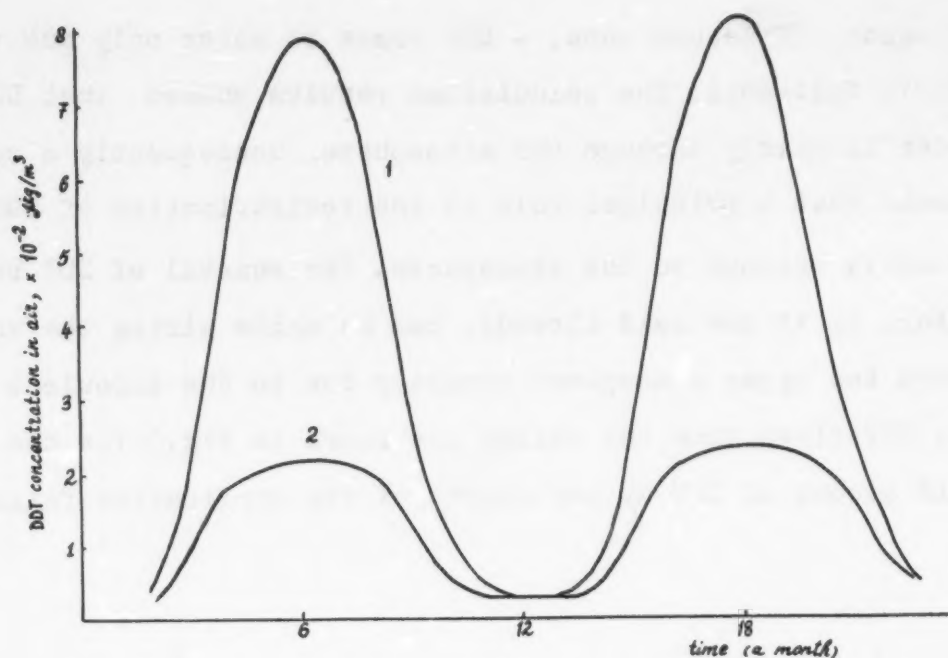


Fig.1. Mean concentration of DDT (aerosols) in the atmosphere.

(1) -  $f_1 = 1$ ,  $K_1 = 10 \text{ m}^2/\text{sec}$ ,  $z^x = 2 \text{ km}$ ;

(2) -  $f_1 = 1$ ,  $K_1 = 1 \text{ m}^2/\text{sec}$ ,  $K_2 = 10 \text{ m}^2/\text{sec}$ ,  $z^x = 0.2 \text{ km}$ ,  
airing is absent.

second case there is no airing, and mixing is much weaker ( $K_1 = 1 \text{ m}^2/\text{sec}$ ,  $K_2 = 10 \text{ m}^2/\text{sec}$ ,  $z^x = 200 \text{ m}$ ). Mean DDT concentrations in the atmosphere in the case of good turbulent mixing is 4 times higher than in <sup>the</sup> case of bad one. It's worth noting that mean concentrations characterize total content in the atmosphere. If pass from mean concentrations to air surface one, we'll find that surface atmospheric concentration of DDT <sup>the</sup> in second case is higher compared with the first one. In order to estimate the role of the atmosphere for DDT dispersion we calculated DDT concentration in water for two cases: <sup>the</sup> in first case DDT was supposed to enter water due to wash-out of soil and due to the atmosphere-

ric fall-outs, <sup>the</sup> in second case, - DDT comes to water only due to the atmospheric fall-outs. The calculation results showed that DDT income into water is mainly through the atmosphere. Consequently a conclusion may be made that a principal role in the redistribution of DDT between various media belongs to the atmosphere. The removal of DDT beyond the valley, as it was said already, can be while airing the valley and across the upper atmosphere boundary due to the turbulent dispersion. DDT flows from the valley are shown in Fig.2 for the case when half amount of DDT at the moment of its application falls out

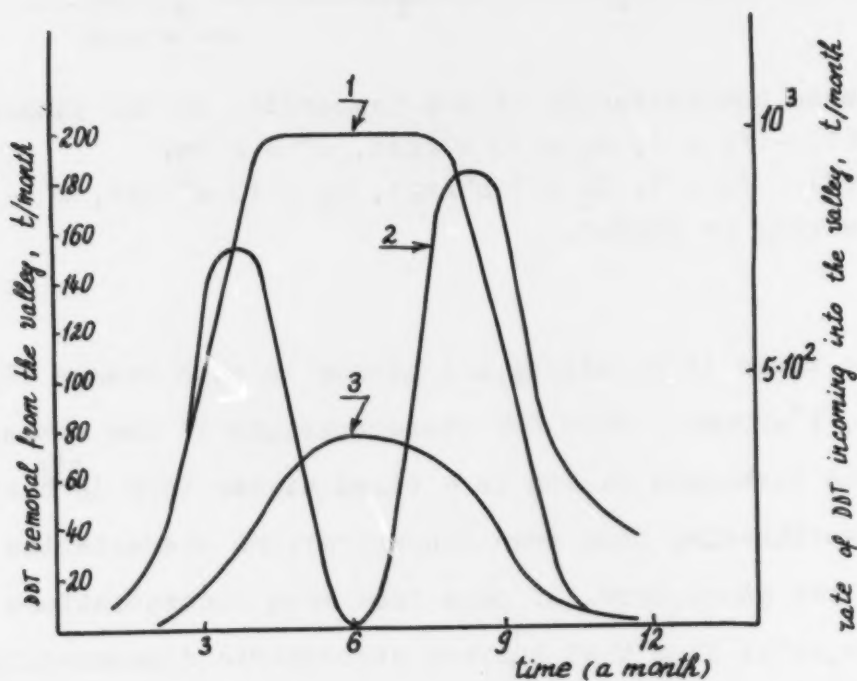


Fig.2. (1) rate of DDT incoming into the valley.  
 (2) DDT removal from the valley when airing.  
 (3) DDT removal across the upper boundary of the valley.



on the fields and half of it enters the valley atmosphere. On the basis of the calculations it follows that DDT removal outside the valley <sup>is</sup> 10% from the used quantity. In conclusion we should like to note, that this model can probably be used to describe pesticide circulation in other regions. The values of a number of parameters should be changed but this will change the general picture of pesticide circulation in the biogeocenosis.

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